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THE

PHYSICAL REVIEW.

THE PHYSICAL PROPERTIES OF SELENIUM.

By P. J. Nicholson.

EVER since the discovery of the sensitiveness of the electrical resistance of metallic selenium to alteration in illumination, attention has been given to the problem of finding an explanation for the phenomenon. In late years, two views have been expressed regarding this. Pfund[1] introduced the idea that the effect is due to a resonance of the electrons in the atom, occasioning explosions which lead to an increase in the number of conducting electrons. This view has found favor with some investigators, particularly with Ries to whom a great amount of valuable work is due. It deserves attention for various reasons: First, the ultimate explanation found must be in terms of the electron theory if that theory is to remain a permanent part of our physical science. Again, the idea of resonance is a very plausible one to explain such an increase of conductivity. The second theory may be construed as quite in harmony with the first. Marc and others have obtained evidence that there exist at least two forms of metallic selenium of widely different electrical resistivity; and it is assumed that illumination brings about a transformation from the less to the more conducting of the two. This theory has been amplified and put in mathematical form by Brown,[2] who assumes the existence of three forms, selenium *A*, *B* and *C*.

As tests of these views, several lines of work suggest themselves, and the object of the present series of experiments was to obtain data that would be of help in the solution of the problem. Since the ultimate explanation must take into account the physical characteristics of the element, one of the first requisites is that satisfactory methods be obtained for the production of good films of selenium in its various forms. Accordingly, the first part of the work had that end in view. In the second

[1] Phys. Rev., XXVIII., 324, 1909.

[2] Phys. Rev., XXXII., 237, 252, 1911.

part, on the other hand, experiments having an immediate bearing on the theories to be tested were taken up.

SPUTTERING OF SELENIUM CATHODES.

There seems to be a great deal that is difficult to determine connected with the sputtering of selenium cathodes. Here, the observations of Longden[1] and later of Pfund,[2] that cathodes of metallic selenium do not yield films in the metallic form, was confirmed. When the current density is very small, films that are very thin but beautiful are yielded. Soon, however, the cathode becomes covered with a black powder which probably is some form of the element; and from that moment, satisfactory sputtering does not take place. Instead of continuous, semi-transparent films, layers appear that are wholly or in part granular in structure.

Since great difficulty has been experienced by different experimenters in obtaining semi-transparent films of metallic selenium by ordinary means, an effort was made to obtain them directly. The method that suggested itself at once was to keep the surface designed to receive the deposit at a temperature of 150° or thereabouts. This was done by using a small furnace of nicrome wire heated by a circuit that was taken through the base of the apparatus and insulated from it. For a variety of reasons, it was found very difficult to keep the pressure constant, and consequently, the temperature would vary. Nevertheless, several deposits were obtained whose surface possessed the appearance of metallic selenium; but their transmission, however, being reddish, showed the presence of some of the amorphous.

Accidentally, several films were obtained directly by sputtering from metallic cathodes which proved to contain at least a large fraction of the metallic form. One layer deposited on a platinum-on-mica grating was both conducting and light-sensitive. As its resistance was about 10^8 ohms, however, the cell was of little use. The conditions necessary for obtaining such deposits were not determined save that the cathode was always a metallic one that had been subjected to long heating near 200°, and that the current density was fairly great. It does not appear probable that this method will be of practical value in view of the ease with which good metallic layers can be obtained by the other process.

Films of amorphous selenium, on the other hand, can be formed by sputtering quite readily; but, if the current density is not very small, the cathode soon changes partly into the metallic state, and thereafter the films are granular, as before. It seemed desirable then to reduce the

[1] American Journ. of Sci., X., 55, 1900.

[2] PHYS. REV., XXVIII., 324, 1909.

heating effect within the apparatus to a minimum. With that end in view, a special cathode sputtering outfit was constructed. This will now be described.

Before the work had proceeded far, it was observed that alternating currents yielded quicker results than direct currents of equivalent voltage. This, no doubt, is due to the fact that the maximum voltage in the former is far in excess of the effective. It appeared better to use alternating current in all further work, but in order to decrease the heating effect, it should be rectified. This suggested the use of a point anode. The cathode was further cooled by a jacket of flowing water.

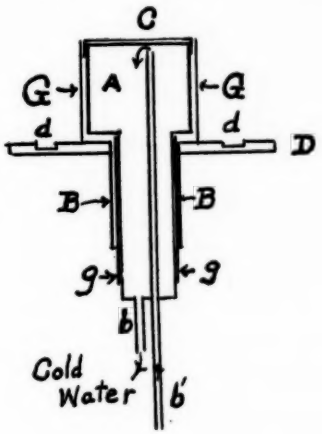

Fig. 1.

Section of cathode sputtering apparatus. *A*, brass chamber, fitted with brass tubes *b*, *b'* through which a steady stream of cold water was forced. *A* was fixed in brass tube *B* with cotinsky cement, and perfect insulation was assured by glass tube *g*. Top of chamber was made very thin and covered with a cap of aluminum foil *C*. Glass tube *G* kept discharge confined to top surface. Small bell-jar, fitted with point aluminum anode, was waxed into groove *d* in brass base *D*. Wire frame supported plate receiving the discharge from 1 cm. to 3 cm. above *C*, while a piece of aluminum foil covered with a layer of selenium was placed on *C*, serving as cathode for the discharge.

All who have ever tried to secure films of selenium by cathode sputtering must have observed that often small portions of selenium fall on the plate receiving the film and become nuclei for beautiful concentric rings which soon form around them. In order to obtain uniform films, then, this effect had to be eliminated; and sputtering upwards[1] was the obvious remedy. The apparatus was found very satisfactory with work on selenium, and moreover, proved to be more satisfactory than the commoner form for obtaining films of other metals. For example,

[1] This had been suggested by Dr. C. M. Sparrow for sputtering substances that cannot be made into continuous cathodes.

by its use, the time consumed in obtaining good mirrors of platinum was reduced by from one half to one third.

The vacuum found most advantageous was such that there was about one centimeter of dark space. As source of voltage a two thousand volt transformer was used. A large resistance was always used in series with the primary so that an E.M.F. of from a few hundred to two thousand volts was available. In no case could the latter be employed, for, as soon as its use was attempted, an emission of gas resulted that caused the pressure to rise above that which the work called for.

By means of this apparatus films of many kinds were obtainable. By using a fairly high current density, almost opaque films of amorphous selenium were deposited in less than one minute. It was found, however, that as a general rule, films deposited quickly were not as transformable as those deposited very slowly.

Other films were obtained that changed into semi-transparent metallic ones and stood long heating at a temperature near 200°. The pure metallic films were very easily distinguished by their plum-colored reflection and the absence of red in their transmission. Films with a good surface, but with some red in their transmission, are quite easily obtainable.

It was found that care should be taken to avoid having any sealing wax inside of the apparatus where the discharge might play on it. In addition to its emission of gas, this substance seems to have a special attraction for the selenium deposits, so that layers of the element accumulate on it in a very short time.

TRANSFORMATION OF THIN FILMS.

Considerable attention was paid to the transformation of selenium films, and this proved to be as enigmatical as the problem of sputtering. The question is here suggested whether transformation into the metallic state is ever complete or not. Some films, of considerable thickness, with beautiful red surfaces, withstood a temperature of 200° for twenty-four hours without showing any sign of transformation. Others would acquire a surface with the familiar plum-colored luster of the metallic selenium but whose transmission contained much red. Occasionally, a film was found which seemed to have transformed completely, having apparently no red transmission. These films were similar to that obtained by Pfund, whose optical constants were measured by him.

Some selenium films seem to vaporize quite readily. These could not be transformed satisfactorily, for it seemed that before transformation was complete, the continuity of the surface was destroyed. Others,

again, changed into the metallic state quite readily, and these stood a heating up to nearly 200° for some hours. The conditions that must be fulfilled in order to transform thin films successfully seem to have partly to do with the process of heating and partly with the nature of the layer. One film on glass, about 2 inches square, was cut into small pieces, and each piece tried came over into the metallic state without difficulty provided the rate of heating was sufficiently slow. This indicates that the character of the films comes into play. All that can be said about the film is that it was yellowish in color, and was obtained when the rate of deposit was fairly slow while the glass plate was at a distance of nearly one inch from the cathode. All films so obtained, however, were not transformed, as the surface soon became broken, as mentioned above. It may be expected that if the pressure on the films were so increased as to cut down vaporization appreciably, transformation could be carried on successfully; and this is to be tested in a later experiment.

Ultra-Violet Absorption.

Several efforts were made to obtain a good semi-transparent film of selenium on quartz, with portions of two different thicknesses, so as to measure the optical constants in the ultra-violet. These, while untransformed, had absolutely no ultra-violet transmission. Although several films on quartz, of one thickness, were transformed, yet success was not met with in transforming films when portions were of different thicknesses. A rough determination of ultra-violet absorption was made, neglecting reflection; but so little of the light could be concentrated on a few square millimeters of film that the thermal couple deflections resulting were very small, and hence, not particularly reliable. It was established beyond doubt, however, that up to 230 $\mu\mu$ the absorption coefficient is not very different from what it is in the blue.

Ultra-Violet Sensibility.

It appears that no quantitative measurements of the sensibility of selenium cells to ultra-violet radiation have ever been made, and it was determined to extend the sensibility curve as far as possible into the region of short wave-lengths. The source of illumination first used was an improved form of water-cooled iron arc designed by Dr. Pfund. This was found to possess such intensity that thermal couple deflections of ten to twenty-five centimeters could be obtained quite readily around 300 $\mu\mu$, while the intensity around 250 $\mu\mu$ was considerable. The arc, however, did not possess the steadiness necessary for this work and it had to give way to a quartz mercury arc, kindly lent by Professor Wood,

to whom I owe my best thanks. As only a small portion of the arc could be concentrated on the spectrometer slit, the intensity obtainable was much smaller than that yielded by the iron arc, but in the matter of steadiness it left nothing to be desired.

The apparatus was set up as in Fig. 2. The lens system L included a water cell that cut out infra-red radiation. Screens and diaphragms cut down all diffused radiation. The concave nickel mirror M_1 focused the light of the quartz mercury arc Q on the vacuum thermal couple T, while the plane nickel mirror M_2 was arranged in a frame in such a way that it could be slid down into the path of the beam so as to divert it on to the selenium cell C. The cell was covered with a piece of crystal quartz cut from a plate, the remainder of which furnished the window of the thermal

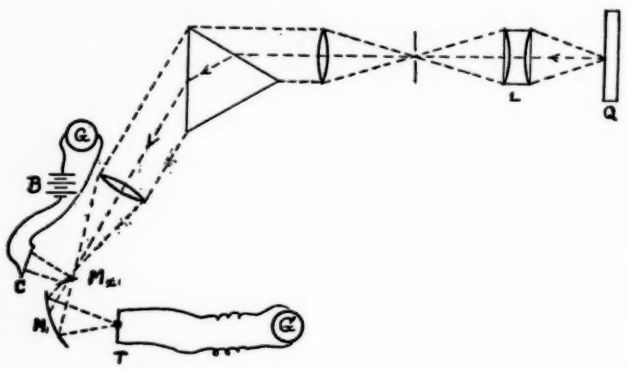

Fig. 2.

couple T. This arrangement insured that the amount of absorption was the same in each case. Experiments were carried out with two cells made by Giltay, and the results found were not essentially different. In each case, the cell was connected through the galvanometer G with a storage battery B of, usually, twelve volts. Torsion was then applied to the galvanometer suspension so as to restore the zero of the instrument to its initial position. Change of conductivity caused by a certain illumination was noted as indicated by the change in galvanometer deflection.

The galvanometer attached to the cell had a sensibility of 1.2×10^{-9}. It was found necessary to introduce a shunt cutting this down by a factor 3 so as to keep the deflections within the desired range. The thermal couple readings were made on the same scale, which was placed at a distance of two meters from the galvanometer.

A vacuum thermal couple was used and the chamber containing the

element was joined to a vacuum[1] tube with charcoal anode, by means of which the vacuum was tested and maintained from time to time. This apparatus was kindly constructed by Dr. Pfund. The galvanometer used was one of the D'Arsonval type, and had a resistance of 20 ohms. This instrument was made by the writer. The sensitiveness of the galvanometer was 3×10^{-9} amperes while a candle placed a meter away from the thermal couple produced a deflection of 24 cm.

Limited exposure of the cell to the radiation was arranged for by using a sector rotated on the axis of the second hand of a small clock, a device used by Pfund in his latest experiments. In the same work, Pfund has shown that Talbot's law is applicable to the selenium cell, and hence, a rotating sector may be used to obtain beams of different energy. In this way, readings for unit, $\frac{1}{2}$, $\frac{1}{4}$ and $\frac{1}{8}$ energy were made. These readings indicated that the deflections for any wave-length obeyed with a very fair degree of accuracy the law

$$d = DI^{\frac{1}{2}}$$

established for the range from blue to yellow by Pfund in the work referred to above. Instead of spending much time in obtaining equal energy deflections in each case, a set of readings was made for every prominent group of lines in the Hg spectrum, using the most convenient energy readings. From these D, the change of conductivity corresponding to unit energy, was calculated, as shown in Curve 1. With each group of lines the maximum deflection for full energy was obtained. The inertia throughout the ultra-violet was observed to be small.

Sensibility Curves with Continued and with Limited Exposure.

Pfund[2] has shown that when selenium cells are exposed to monochromatic light for 12.5 sec., d, the increase in conductivity, varies with I, the intensity of the illumination, according to the law

$$d = DI^{\beta},$$

where D is a constant for any particular wave-length. β was found to be very nearly $\frac{1}{2}$ for regions of the spectrum from the violet to the yellow. As the red is approached, however, β increases; so that with deep red and infra-red $\beta = 1$. For the shorter wave-lengths, this agrees with the results found by Rosse, Adams and Berndt. This relation was tested from 230 $\mu\mu$ to 900 $\mu\mu$ and found to hold with a fair degree of accuracy.

Most of these experiments, however, were carried on in mid-summer in Baltimore, where the temperature was very high, with very consider-

[1] See Pfund, Phys. Rev., XXXIV., 370, 1912.

[2] Phys. Rev., XXXIV., 370, 1912.

able variations and with great humidity. The results so obtained are accordingly not so reliable as would have been found under more favorable circumstances, and their agreement is not so good. Pfund, on the other hand, worked in winter, in a room in which the temperature was kept constant to one tenth of a degree. Changes in temperature are known to affect cells very markedly, while the observations of Ries and others indicate the dependence of cells on humidity. The Giltay cells are put up so that there is absolute communication between the outside air and the selenium surface, hence the variations. One cell was enclosed in an airtight box, with glass window, after it had been dried thoroughly, and thereafter it showed a marked improvement in its behavior.

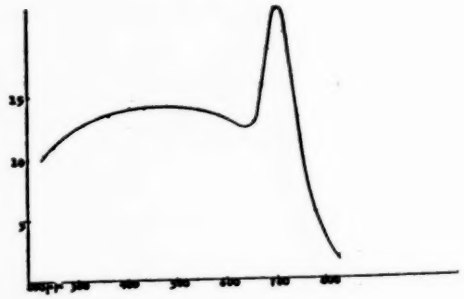

Fig. 3.

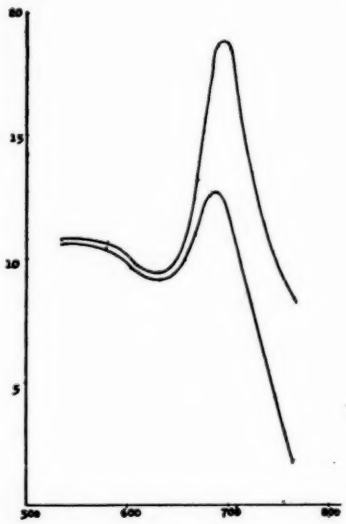

Fig. 4.

Curve 1. Sensibility of the Giltay cell extended into the ultra-violet. E.M.F. on cell, 12 volts. Time of exposure, 12½ seconds. Ordinates represent change of conductivity in terms of galvanometer deflections.

Curve 2. Showing sensibility when time of exposure was 15 seconds contrasted with the corresponding sensibility when time of exposure was unlimited. This shows the increase of inertia with the wave-length.

For the 12.5 sec. exposures the observations of Pfund were fully verified. The region in which the deflection varies as the square-root of the incident beam was found to extend into the ultra-violet, as far back as 230 $\mu\mu$. When the time of illumination was reduced to 10 sec., a noticeable increase in the value of β followed, with a small shift of the region in which β becomes 1 towards shorter wave-lengths. With the longer illuminations (15 and 20 sec.) the contrary was the result, as might be

expected. Finally, with exposure until a steady state was reached, it was found that β was approximately constant and equal to .5 throughout the entire spectrum. There appeared, however, to be an appreciable minimum in the value of β about the region 600 $\mu\mu$, for here the value found in many sets of readings was about .4. The variation involved, however, may be seen to be comparatively small when we consider that it can be accounted for by a variation of less than 7 per cent. in one of the readings of deflection on which the value of β is based. The difficulties mentioned above make themselves particularly manifest here since the intervals between readings varied from about two minutes in the violet to from ten to twenty minutes in the infra-red; and as a result, conditions had an opportunity of changing very considerably during that time. If the interval between readings is not sufficiently long, fatigue makes itself manifest and the readings are affected. Curve 2 illustrates the difference between 15 sec. exposure and unlimited exposure.

Variation of Inertia with Wave-Length.

Fig. 4 shows that there is a very marked difference between the inertia of the red and infra-red as compared with the rest of the spectrum. It would be better, however, to show graphically the time required to reach say $\frac{3}{4}$ of saturation value of deflection in different parts of the spectrum, and this will be done shortly. The difference between the full deflection and that after a limited exposure is, apparently, constant from 230 $\mu\mu$ to near 700 $\mu\mu$; but here it very suddenly increases until it attains a value many times greater than before. The exact difference varies somewhat, corresponding to humidity and temperature, and very markedly to fatigue when the cell has not been allowed a sufficient rest between readings: but the general facts are always the same. This difference between the action of different parts of the spectrum led to the following experiments, suggested by Dr. Pfund.

Effects Due to a Steady Illumination Using Beams for which k is nearly Constant.

The cell was subjected to a steady illumination, first of green light, and again of deep red, and, finally, of infra-red, and sensibility curves were taken as before. This was brought about by obtaining a parallel beam of light from a Nernst glower, and throwing it on the cell by means of a right-angled prism, through a window on the apparatus covered by an absorption screen. As is the case when the current passing through the cell is great owing to a high E.M.F., so it was found here that the conductivity of the cell was very unsteady when it had been increased five

to ten times by illuminating it. It was, accordingly, found necessary to interpose an inclined piece of plate glass in the path of the beam so as to cut down the conductivity to the desired degree.

In one experiment with cell No. 2, the conductivity was increased about three times by means of a beam of red light. The absorption cell used was composed of equal parts of a 10 per cent. solution of sodium bichromate and a 1 per cent. cyanine solution. This had a slight transmission throughout the spectrum but only a very little up to 710 $\mu\mu$. The results found can be summed up by saying:

1. The sensibility from the violet to the orange was slightly decreased. The red maximum, however, was almost entirely cut out, and the cell became practically insensitive at about 750 $\mu\mu$.

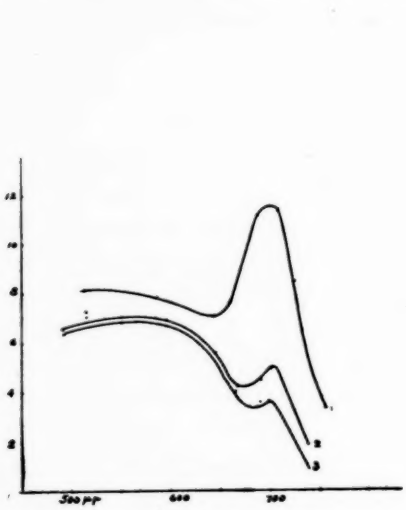

Fig. 5.

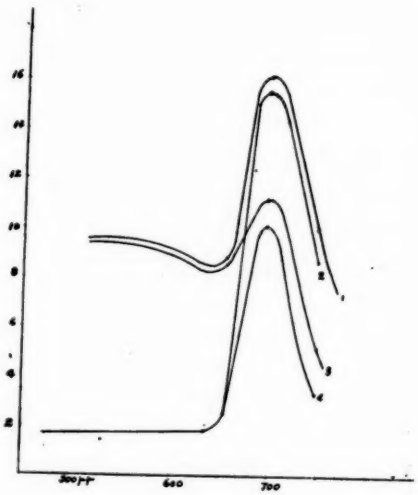

Fig. 6.

Curve 3. Cell subjected to a steady infra-red beam that increased its conductivity 2½ times. 2 and 3 show sensibility with unlimited and 15 sec. exposures, respectively. 1 gives corresponding ordinary sensibility curve.

Curve 4. Cell subjected to steady beam of green light that increased its conductivity 3 times. 2 and 4 show sensibility with unlimited exposures and 15 sec. exposures, respectively. 1 and 3 show corresponding ordinary curves. Cell unsteady. Inertia very marked in red and infra-red.

2. The inertia of the cell was very markedly decreased.

A second absorption cell whose transmission was strictly confined to the infra-red from 800 $\mu\mu$ to 1,950 $\mu\mu$, was then used. This cell consisted of equal parts of a .6 per cent. solution of naphthol green and a 1 per cent. cyanine solution. The amount of radiation transmitted was such as to increase the conductivity about 2.5 times. The results here differed

very little from those obtained using the red cell, save that the red maximum was cut out more completely and that the sensibility extended a little less far towards the infra-red. The results of this experiment are shown by Curve 3.

Finally, experiments were carried out using a saturated solution of copper chloride for the absorption cell. The transmission of this cell was not accurately determined; but it is well known that such solutions have a maximum transmission in the green while they are opaque to wave-lengths longer than .65 μ. The conductivity was now increased to three times its original value. The results that followed are shown in Curve 4, and were quite different from those hitherto obtained, for:

1. The sensibility was reduced almost to nil on the shorter wave-length side of the red maximum. The red maximum itself was reduced slightly as was the infra-red sensibility.

2. Inertia was quite marked.

Röntgen Rays.

To test further the laws stated above experiments were performed using Röntgen rays as exciting source.

To cut down the intensity of the rays by definite steps, a large rotating sector of heavy sheet lead was made. The quartz window of the cell was replaced by one of aluminum foil. By actual test, with the Röntgen ray tube in the position which it occupied throughout the experiment, the lead was of such thickness as to shield off all effects due to the rays.

A second piece of sheet lead was mounted in front of the rotating sector so as to allow only a narrow beam to strike the cell. The sector was rotated by means of an electric motor whose speed was quite high. By sliding the motor on its support, any portion of the sector could be brought in front of the hole in the lead sheet so that full, three quarters, one half or one quarter the intensity of the beam could fall on the cell.

As observed by other experimenters, the effect of Röntgen rays on the cell proved to be very slow. This rendered it an easy matter to take a reading with considerable accuracy when the exposure was of limited duration. Of course it was necessary that there should be two observers; one to observe the time, and the other to read the deflection of the galvanometer.

The results obtained from this experiment differ but little from those obtained using the long wave-lengths. With short exposures, an approximate first power law held. Exposure until a steady deflection was reached required a wait of from 15 to 30 minutes for each reading, and a still longer wait for recovery of the cell. The results indicated an

approximate square root law as the following set of readings will show:

Intensity of Rays.	Deflection after 15 Sec.	Maximum Deflection.
1	3.40	11.50
2	7.70	17.00
4	15.30	24.10

ABSENCE OF SELECTIVE EFFECT.

The work of Pohl and Pringsheim on the external photoelectric effect of the alkali metals has shown that this effect depends on whether the incident light is polarized, and on the plane of polarization. Ries has found that the internal effect in selenium shows no such peculiarity through an experiment in which he allowed polarized light to fall on a cell at an angle of 45°, and observed that the deflections were of equal magnitude regardless of direction of current. A direct test of this had been made before the work of Ries was published.

A Nicol prism was introduced between the pair of lenses that focused the light of the Nernst glower on the slit of the spectrometer. A series of readings was taken throughout the visible spectrum, with the light polarized first in the plane of incidence, and then perpendicular to that plane. Suffice it to say that at no wave-length could a difference be detected between the deflection due to a given amount of energy, whether polarized in a particular plane or not. It is possible, however, that roughness of the selenium surface destroyed the polarization of the light; and to obviate this difficulty the experiment is to be undertaken with cells having mirror surfaces obtained by cathode sputtering. This observation may or may not have some value from a theoretical point of view; at any rate it seems desirable to place on record the fact that it was made.

THEORETICAL.

In the following pages an effort is made to calculate on the basis of the electron theory, the various effects that should be expected on the hypothesis put forward by Pfund that the increase of conductivity is an internal photo-electric effect. At best, such a theory can be only approximate, if extraordinary complications would be avoided. In the development of the equations, it is found necessary to leave out of account such effects as the following:

1. Variation in the coefficient of recombination. In view of the work of Plimpton[1] it is highly probable that this quantity is subject to large variation while selenium is undergoing changes due to illumination of varying intensity.

[1] American Jl. of Sci., XXXV., 39, 1913.

2. Diffusion of the electrons. If an appreciable amount of diffusion does exist, the expression developed for the number of electrons present in a layer is inaccurate. Many experiments have shown that the absorption coefficient of metallic selenium is very high. If we take $k = 6 \times 10^4$ as the average value in the visible spectrum as obtained by Pfund, we see that the intensity of a beam of light is reduced to 1/1,000 of its initial value after penetrating

$$\frac{\log 1{,}000}{6 \times 10} = 1.1 \times 10^{-4} \text{ cm.}$$

If diffusion is not very large, then, the effective depth of penetration of the light must be much smaller than this thickness. Brown[1] has deduced from his observations that the effective depth is 1.4×10^{-3} cm. for the Giltay cell, and if his assumptions are correct, diffusion must be a large factor. Further experiments relating to this point are under contemplation.

3. "Skin effect," owing to possible thinness of layer affected by light. It is possible, however, that no serious complication would enter from such a source, as the effect would be to bring in a constant factor in the relation between number of electrons present and current flowing.

4. Variation of coefficient of absorption when conductivity is increased. Such a variation would be expected on the electron theory. However, Amaduzzi[2] found no variation in the emissivity when selenium was illuminated, and Pfund, in an unpublished research, using elliptically polarized light, could detect no change in the optical constants when the metal was illuminated by a second beam of very great intensity. This effect, if it exists, must be very small.

5. Non-uniform distribution of electrons while selenium is in the dark. It is quite probable that the density of the electrons very near the electrode is greater than elsewhere. However, this would probably introduce no serious complication.

6. Losses of electrons due to external photoelectric effect. This[3] effect is probably very small, particularly in the visible spectrum.

7. Secondary ionization.[4]

This treatment may not be fundamentally different from that which assumes chemical effects as the cause of transformations which take place in the selenium; for such transformations, in so far as they cause an increase of conductivity, mean simply a liberation of electrons. The equa-

[1] PHYS. REV., XXXIV., 201, 1912.

[2] Accad. Lincei, XVII., 590, 1908.

[3] See Amaduzzi, Rend. di R. Accad. Bologna, XIV., 39, 1910.

[4] See Robinson, Phil. Mag., XXV., 115, 1913.

tions here given, however, possess the advantage of being in terms of quantities which have a definite physical meaning, not one purely arbitrary constant entering into the system. Accordingly, a field is opened for experimental tests which should be capable of either disproving or verifying the theory proposed.

THE VARIATION OF CONDUCTIVITY WITH INTENSITY OF ILLUMINATION.

Consider a layer of selenium whose depth is s and whose area is A. Let N denote the density of the electrons in it while in the dark. Let M^2 denote the number of electrons produced per second in unit volume, while in the dark. There will be present NsA electrons in the whole layer, and, if α^2 denote the coefficient of recombination, we have, while the selenium is illuminated

$$M^2 = \alpha^2 N^2; \quad \text{or} \quad M = \alpha N.$$

Let I denote the intensity per unit cross section of a uniform monochromatic beam of light passing normally into the surface of the selenium. Of this amount Ie^{-kx} will reach a layer a distance x from the surface, k being the coefficient of absorption. $Ie^{-k(x+dx)}$ will pass out through a surface a distance $(x + dx)$ from the top. Then j, the amount of light absorbed in the layer of thickness dx just considered, will be

$$j = AIe^{-kx} - AIe^{-k(x+dx)} = AIe^{-kx}(1 - e^{-kdx}) = AIke^{-kx}dx.$$

It is reasonable to suppose that the number of electrons expelled from their atoms due to resonance will be proportional to j—say $\mu j = \mu AIke^{-kx}dx$. There will also be a spontaneous expulsion of electrons amounting to AM^2dx in this layer whether the surface be illuminated or not. If n represents the density of the electrons in the layer there will be a loss of α^2n^2Adx due to recombination. The total change per second in the number of electrons present in the layer will be

$$\frac{d}{dt}(nAdx) = AM^2dx + \mu AIke^{-kx}dx - \alpha^2n^2Adx$$

So that

$$\frac{dn}{dt} = M^2 + \mu kIe^{-kx} - \alpha^2n^2 \qquad (1)$$

$$= M^2 + c^2e^{-kx} - \alpha^2n^2,$$

$$= q^2 - \alpha^2n^2,$$

c and q being introduced to reduce the mathematical complication.

The solution for this equation may be put in this form:

$$n = \frac{q}{\alpha}\left\{ 1 - \frac{2}{\frac{q+M}{q-M}e^{2\alpha qt} + 1} \right\}. \tag{2}$$

Now, if we denote the total number of electrons present in the whole body by m, we have

$$m = \int_0^\infty Andx = -A\int_{(c^2+M^2)^{\frac{1}{2}}}^{(c^2e^{-ks}+M^2)^{\frac{1}{2}}} \frac{q}{\alpha}\left\{ 1 - \frac{2}{\frac{q+M}{q-M}e^{2\alpha qt} + 1} \right\}\frac{2qdq}{q^2-M^2}.$$

It is seen immediately that the steady state following illumination, corresponding to $t = \infty$, is given by the first term of the integral. The second term is quite difficult to integrate; but an approximation to its value can readily be obtained if we consider the state of affairs when t has a considerable value. Then the term can be developed into a very rapidly converging series, of which the first term alone need be considered, so that

$$m = \frac{2A}{\alpha k}\int_{(c^2+M^2)^{\frac{1}{2}}}^{(c^2e^{-ks}+M^2)^{\frac{1}{2}}} \left\{ \frac{-q^2dq}{q^2-M^2} + \frac{2q^2}{(q+M)^2}e^{-2\alpha qt}dq \right\} \tag{6}$$

$$\begin{aligned} = \frac{2A}{\alpha k}\Big[&(c^2+M^2)^{\frac{1}{2}} - (c^2e^{-ks}+M^2)^{\frac{1}{2}} + \frac{M}{2}\log\frac{M+(c^2e^{-ks}+M^2)^{\frac{1}{2}}}{M-(c^2e^{-ks}+M^2)^{\frac{1}{2}}} \\ &\times \frac{M-(c^2+M^2)^{\frac{1}{2}}}{M+(c^2+M^2)^{\frac{1}{2}}} \\ &- \frac{(c^2e^{-ks}+M^2)}{\alpha t\{(c^2e^{-ks}+M^2)^{\frac{1}{2}}+M\}^2}e^{-2\alpha t(c^2e^{-ks}+M^2)^{\frac{1}{2}}} \\ &+ \frac{(c^2+M^2)}{\alpha t\{(c^2+M^2)^{\frac{1}{2}}+M\}^2}e^{-2\alpha t(c^2+M^2)^{\frac{1}{2}}}\Big], \end{aligned} \tag{7}$$

neglecting all terms involving the factor $e^{-4\alpha qt}$; and since the quantity e^{-ks} is vanishingly small for cells that are opaque

$$\begin{aligned} m = \frac{2A}{\alpha k}\Big[&\left\{ (c^2+M^2)^{\frac{1}{2}} - M + \frac{M}{2}\log\frac{c^2}{4M^2}\cdot\frac{M-(c^2+M^2)^{\frac{1}{2}}}{M+(c^2+M^2)^{\frac{1}{2}}} + \frac{M}{2}\cdot ks \right\} \\ &- \frac{1}{\alpha t}\left\{ \frac{1}{4}e^{-2\alpha Mt} - \frac{c^2+M^2}{\{(c^2+M^2)^{\frac{1}{2}}+M\}^2}e^{-2\alpha t(c^2+M^2)^{\frac{1}{2}}} \right\}\Big]. \end{aligned} \tag{8}$$

After steady state has been reached, *i. e.*, when $t = \infty$, the second term has vanished. Of the first term, the quantity

$$\frac{2A}{\alpha k}\cdot\frac{Mks}{2} = \frac{MAs}{\alpha} = NAs$$

obviously represents the total number of electrons present when cell is in the dark. The increase in the number of electrons owing to illumination of intensity I then is

$$m - m_0 = \frac{2A}{\alpha k}\left[(c^2 + M^2)^{\frac{1}{2}} - M - \frac{M}{2}\log\frac{c^2}{4M^2}\cdot\frac{M + (c^2 + M^2)^{\frac{1}{2}}}{M - (c^2 + M^2)^{\frac{1}{2}}}\right]. \quad (9)$$

If M is very small as compared with c this reduces to

$$m - m_0 = \frac{2Ac}{\alpha k} = \frac{2A\sqrt{\mu k I}}{\alpha k} = \frac{2A}{\alpha}\sqrt{\frac{\mu I}{k}}. \quad (10)$$

As M increases in value, the proportionality between $m - m_0$ and c becomes less and less accurate.

Now, let us consider the relative value of c and M in a practical case. The number of electrons ejected by light of intensity I, according to our assumption, in an opaque layer is

$$\int_0^\infty k\mu I e^{-kx}dx = \mu I = \frac{c^2}{k}.$$

The number of electrons ejected, as indicated by the increase in conductivity, is usually of the same order of magnitude as the number produced spontaneously whether the cell is illuminated or not. Hence c^2/k is of the same order of magnitude as M^2. But, as seen, k is a very large number; hence c^2 is large compared with M^2, and in many particular cases, c will be large compared with M. We should, therefore, expect proportionality to exist between the increase in conductivity and the square root of the intensity of illumination, *i. e.*,

$$d = D\sqrt{I}.$$

This is the law verified by Rosse, Pfund, Adams, Berndt and the writer. It must be borne in mind, however, that D involves the coefficient of absorption, k, as well as μ, both of which are functions of the wavelength; hence the law will not hold for unresolved or partially resolved light. A different relation, therefore, should be expected for every source of unresolved light used. In order to obtain a complete expression connecting change of conductivity, intensity of illumination, and wavelength, it is necessary only to express μ and k as functions of the wavelength, correct I for loss of reflection, and insert its value in the equation. This problem does not at all seem hopeless.

Dependence of Sensibility on Dark Conductivity.

Referring to equation (9) it can readily be seen that $m - m_0$, to which the increase in conductivity is proportional, decreases as M increases.

Hence, for cells of high resistance, high sensibility would be expected. This, as a rule, is true of selenium cells. Assuming μ to be constant when the temperature is varied, we should expect a change in sensibility corresponding to temperature changes in resistance. Now μ should measure the external photoelectric effect, and this has been shown to be independent of temperature in the case of good conductors. The work of Amaduzzi[1] indicates a decrease of photoelectric effect of selenium with rising temperature, but his experiments were not carried below ordinary temperatures. However, if μ has not increased very markedly when the resistance is increased by lowering the temperature, we should expect a large increase in sensibility. This was verified by Miss McDowell[2] with a number of cells whose resistance increased several hundred times when their temperature was lowered to that of liquid air.

An experiment performed by Pochettino[3] does not admit of so ready an explanation, however. This physicist used a cell whose resistance fell very noticeably when its temperature had been lowered; but its sensibility increased somewhat, nevertheless. Cells whose resistance decreases at low temperatures are rather unusual, and to explain this effect a change in α, k or μ must be assumed.

LIGHT-NEGATIVE SELENIUM.

Similar considerations lead to a possible explanation of light-negative selenium. We have, when steady state is reached,

$$m = \frac{2A}{\alpha k}\left[(c^2 + M^2)^{\frac{1}{2}} - M - \frac{M}{2}\log\frac{c^2}{4M^2}\cdot\frac{M + (c^2 + M^2)^{\frac{1}{2}}}{M - (c^2 + M^2)} + \frac{Mks}{2}\right]. \quad (11)$$

It is seen by substituting for c values of the same order of magnitude as M that the first term, representing the sensibility, is now small, while the last term, which represents the dark conductivity, is large. Now, if through the action of light α increased slightly, so that the second term would be slightly decreased, that decrease could easily be of such magnitude as to more than compensate for the first term which represents the change due to illumination. The latest work[4] on the value of α for gases indicates that when the distribution of ions is not uniform α is very much greater than it is for a uniform distribution. The impinging of light on selenium violently disturbs the distribution of electrons in the element; hence, an increase in a is plausible. Effects of this kind could not be expected to be great in agreement with the fact that the sensibility of light-negative selenium has always been found to be very small.

[1] Rend. di R. Accad. Bologna, XIV., 39, 1910.
[2] PHYS. REV., XXXI., 524, 1910.
[3] Rend. R. Accad. dei Lincei, XI., 286, 1904.
[4] Plimpton, American Jl. of Sci., XXXV., 39, 1913.

INERTIA.

We next consider the case when t has a considerable value, but a steady state has not been reached. In such a case we have the additional term

$$\frac{2A}{\alpha^2 kt}\left\{\frac{c^2+M^2}{\{(c^2+M^2)^{\frac{1}{2}}+M\}^2}e^{-2\alpha t(c^2+M^2)^{\frac{1}{2}}}-\tfrac{1}{4}e^{-2\alpha Mt}\right\}. \qquad (12)$$

The quickness with which a steady state is reached depends on the quickness with which these terms disappear. Hence the inertia of a cell on illumination is seen to depend on the three coefficients,

$$\frac{I}{\alpha^2 k}, \quad \frac{I}{\alpha(c^2+M^2)^{\frac{1}{2}}}=\frac{I}{\alpha(\mu kI+M^2)^{\frac{1}{2}}} \quad \text{and} \quad \frac{I}{\alpha M}.$$

We should expect, then, that the rate at which a maximum deflection is approached should be:

1. Least for regions of smallest absorption. This is a well-known fact, verified throughout the present work. This also explains the slow action due to Röntgen rays.

2. Least when illumination is faintest. This has been mentioned by Pfund, Miss McDowell and others, and observed by the writer again and again.

3. Least for least value of dark conductivity. This was verified by Miss McDowell,[1] who found that the action at liquid air temperatures, where the dark conductivity is very low, became very sluggish.

POSSIBLE EXPLANATION OF ANOMALOUS EFFECTS.

We have seen that in ordinary experiments c is great compared with M; hence, the effect of the second term in equation (12) will be manifest long after that due to the first. When t is very small, however, the latter is the greater term. The quantity M, on the other hand, is widely different for different preparations, from the light-negative variety up to Ruhmer's soft and hard selenium. With a suitable choice of M the first term could be made to predominate for a moment. Under such conditions, we should expect a maximum deflection to be reached in an instant, followed by a slow decrease. Effects of this kind have been observed since the earliest work done on the element.[2]

DECREASE OF INERTIA WITH STEADY RED ILLUMINATION.

An explanation of the disappearance of inertia due to red light when a cell is illuminated steadily with light of shorter wave-length can be

[1] PHYS. REV., XXXI., 524, 1910.

[2] Ries, Die elektrischen Eigenschaften und die Bedeutung des Selens für die Elektrotechnik, p. 27.

obtained from similar considerations. Such an explanation is attempted in preference to a complete mathematical deduction owing to the great complications that arise in the solution of the equations. Here, steady illumination of the cell may be considered, on the average, with certain limitations, as being equivalent to a large increase in M. When the change in conductivity due to the incidence of a small amount of red light is then considered, we have the exponent of the first term small, since

$$c = \sqrt{k\mu I}$$

and μ is most probably small in regions of long wave-length. The two terms would, therefore, approach one another in value, so that the effect of both would be expected soon to disappear. On the other hand, the fact that μ and k are large for regions of shorter wave-length may explain satisfactorily the fact that there is no appreciable change in inertia in these regions.

EFFECT OF STEADY ILLUMINATION BY APPROXIMATELY MONOCHROMATIC BEAM ON SENSIBILITY.

This theory is capable of development for the case just discussed when there is a steady illumination on the cell while its sensibility curve is taken. For this case the equations become extremely complicated and nothing is gained by reproducing them since a few simple considerations are sufficient to explain the facts. First, considering the case when there is a steady green illumination. As seen, we have the approximate law

$$d = D\sqrt{I},$$

D being a function of k and μ. Hence,

$$\frac{d}{dI}d = \frac{1}{2}\frac{D}{\sqrt{I}},$$

so that the sensibility to a given amount of illumination decreases as the total illumination is increased. If μ and k were constant, we should expect this decrease to be manifest throughout the spectrum, regardless of the steady illumination on our cell. But, as seen, D involves μ and k, both of which are functions of the wave-length. In regions of shorter wave-length, k being approximately constant, sensibility should disappear. In the regions of long wave-length, on the other hand, k is small. As a consequence, red light falling on a cell illuminated by green light will penetrate into its interior, to parts unaffected by green light, hence giving rise to an increase of conductivity that is almost unaffected by the presence of the green illumination.

When the cell is subjected to a steady beam of light whose coefficient of absorption is small while its sensibility is measured, the case is quite different. Obviously, the sensibility to light whose absorption is approximately the same as that of the steady beam will be very small, provided the value of μ is not very different. When a beam of light of shorter wave-length falls on such a cell, its action will be confined to a thin layer; but μ being tremendously greater here, the effect of the steady beam is hardly appreciable. This explains the retention of the blue and green sensibility when a cell is subjected to a steady beam of red or infra-red radiation.

INITIAL RATE OF CHANGE OF CONDUCTIVITY DUE TO ILLUMINATION.

Having discussed the rate of increase of deflection after light has been falling on the cell for a considerable length of time, but before the steady state is reached, it remains for us to discuss the initial rate of change. We have

$$\frac{dm}{dt} = -\frac{2A}{\alpha k}\frac{d}{dt}\int_{(c^2-M^2)^{\frac{1}{2}}}^{(c^2e^{-kz}+M^2)^{\frac{1}{2}}} \left\{\left(1 - \frac{2}{\frac{q+M}{q-M}e^{2\alpha qt}+1}\right)\frac{q}{(q^2-M^2)}\right\} dq$$

which becomes, when $t = 0$,

$$= -\frac{8A}{k}\int_{(c^2+M^2)^{\frac{1}{2}}}^{(c^2e^{-kz}+M^2)^{\frac{1}{2}}} \frac{q^3(q+M)(q-M)^2\,dq}{(q-M)(q+M+q-M)^2(q^2-M^2)}$$

$$= \frac{A}{k}c^2 = A\mu I.$$

The initial rate of change of conductivity is, therefore, proportional to the intensity of the incident beam.

If the time considered after incidence of light on the cell be small compared with the time required to reach a maximum deflection, we should expect the change of conductivity to be approximately proportional to the intensity. When the light used is of long wave-length, or when the intensity of the beam is very small, while time of exposures is about ten seconds, then, this relation would be expected to hold. This explains the first power law established by Pfund in regions of great wave-length. Stebbins[1] assumes the same relation in his work on stellar photometry, where the intensities used were very small, and, no doubt, the law was verified by him for such cases.

[1] Astrophys. Jl., XXXII., 185, 1910.

Recovery.

To find the expression representing the recovery of selenium, we proceed as follows:

When the illumination is cut off, there will still be produced M^2 electrons per unit volume per unit time. The rate of recombination will remain as before. Representing the density of electrons by n, as before, we have

$$\frac{dn}{dt} = M^2 - \alpha^2 n^2,$$

for which we have the solution

$$n = \frac{M}{\alpha}\left\{ 1 - \frac{2}{\frac{M+N'}{M-N'}e^{2\alpha Mt} + 1} \right\},$$

where N' denotes density of the electrons when $t = 0$, *i. e.*, when selenium was in a steady state under illumination.

Now, glancing at a previous equation we see that

$$N' = \frac{q}{\alpha} = \frac{1}{\alpha}\{c^2 e^{-kz} + M^2\}.$$

Having substituted this value and introduced a number of obvious approximations we obtain the solution in the form

$$m = NsA + \frac{4AM}{\alpha k}\left\{ 2\log\frac{M\alpha + (c^2+M^2)^{\frac{1}{2}}}{M\alpha + M}e^{-2\alpha Mt} - \frac{ks}{2}\left(\frac{1}{2} - \frac{1}{\alpha}\right)e^{-2\alpha Mt} + \frac{1}{\alpha}\log\frac{c^2}{4M}\cdot\frac{M + (c^2+M^2)^{\frac{1}{2}}}{M - (c^2+M^2)^{\frac{1}{2}}}e^{-2\alpha Mt}\right\}.$$

The deductions to be made from this are not greatly different from the results of the former equation, viz.,

1. Rate of recovery greatest when absorption is greatest, amply verified by experiment.

2. Rate of recovery greatest for great values of I and μ.

3. Rate of recovery greatest with cells of high conductivity, a fact often observed and verified by Miss McDowell in her low temperature experiments.

Glancing at the terms involving t, we see that that quantity appears only in the expression $e^{-2\alpha Mt}$. Moreover, this quantity is associated with coefficients of considerable magnitude. Turning to equation (8) on the other hand, we see that the term controlling the time required to reach

a steady state under illumination is $\frac{I}{2\alpha^2 kl} e^{-2\alpha M t}$. The latter, therefore, disappears much more quickly than the former. This is in agreement with experiment, for it is well known that it takes a longer time to return to the initial conductivity after a cell has been illuminated than it does to reach a steady state under illumination.

Bearing on Effective Depth of Penetration.

The agreement between the above deductions and experiment indicates that the view expressed is correct that μ increases with decreasing wave-length. The only experimental evidence on this point is the work of Amaduzzi[1] who found that μ had a value in the ultra-violet but that it was too small to be measured in the visible spectrum. As seen, the approximate sensibility law is

$$d = D\sqrt{I},$$

where D is a function only of μ, α, and k. Moreover, k is nearly constant on the short wave-length side of 550 $\mu\mu$. This law would, accordingly, require a steady increase of sensibility as μ increased, and this is not borne out by experiment. It would seem, then, that a factor not taken into account in the above discussion enters into the problem. This strengthens the view of Pfund that the effective depth of penetration is so small here that Ohm's law fails to hold and it is necessary to introduce an undetermined factor in the relation between conductivity and number of electrons present.

Time Taken in Reaching a Steady State.

The equations given above fail to represent the facts concerning the time taken to reach a steady state under illumination. The equations would indicate that this should be extremely short—less than a second, in an average case, probably. As a matter of fact, the time required by a selenium cell to reach a steady state is considerable, varying from about 20 seconds to several hours. It is probable that a distinction should be made between lag proper to the selenium owing to the change in conductivity caused by the illumination and the lag, due to Joule heating, and potential effects. At best, however, a considerable disparity exists on this point. A plausible explanation of it may be found in the fact that diffusion has been neglected in the development of the equations. Even if diffusion were so small that its effect had little influence on the general conclusions derived from the equations, it is quite possible that,

[1] Rend. di R. Accad. Bologna, XIV., 39, 1910.

if its influence be taken into account in the latter, the time required to reach a steady state would be found to be lengthened considerably.

When this factor is taken into account, equations result as given below, for which a solution has not yet been obtained. Let n' denote density of atoms that have lost an electron, and C, the coefficient of diffusion of electrons. The reasoning used above will apply here, so that we have

$$\frac{\partial n'}{\partial t} = M^2 + c^2 e^{-kx} - \alpha^2 n n'.$$

For electrons the equation will be somewhat different. $AC(\partial n/\partial x)$ electrons will enter the layer considered above through the top surface, in unit time. $AC[(\partial n/\partial x) + (\partial^2 n/\partial x^2)dx]$ will pass through the lower surface. The layer will gain, accordingly, $-AC(\partial^2 n/\partial x^2)dx$ electrons in one second, and we should have

$$\frac{\partial n}{\partial t} = M^2 + c^2 e^{-kx} - \alpha^2 n n' - C\frac{\partial^2 n}{\partial x^2}.$$

Summary.

1. Considerable information has been collected regarding the sputtering of selenium cathodes, and an improved form of sputtering apparatus has been used.

2. Many semi-transparent films of amorphous selenium have been transformed into the metallic state.

3. The ultra-violet absorption of metallic selenium was roughly determined.

4. Selenium cells have been found to retain a large sensibility down to 230 $\mu\mu$, and the sensibility curve for short wave-lengths was determined.

5. Sensibility curves were obtained when exposure was limited and of varied duration, as well as when steady state was reached. If change in conductivity be represented by d, energy of incident beam by I, while β and D are constants, the law $d = DI$ was found to hold with considerable accuracy in every case. When exposure is between 12.5 sec. and 20 sec. Pfund's results are confirmed that $\beta = 1$ in red and infra-red but $\beta = \frac{1}{2}$ for shorter wave-lengths. For unlimited exposures it was found that $\beta = \frac{1}{2}$ throughout the spectrum.

6. Sensibility curves were obtained with a cell permanently exposed to illumination of different wave-lengths, and different peculiarities were noted.

7. The law $d = DI^\beta$ was found to hold with considerable accuracy when the exciting source was Röntgen rays. For short exposures, $\beta = 1$, while $\beta = \frac{1}{2}$ when time of exposure is unlimited.

8. Experiments conducted with home-made cells indicate that they obey the same laws as the Giltay cell.

9. A mathematical deduction has been made, with the electron theory as a basis, from which the most important facts known regarding the behavior of selenium cells have been deduced. The facts accounted for are as follows:

(*a*) Variation of change in conductivity with square root of intensity for long exposures.

(*b*) Variation of change in conductivity directly with the intensity when time of illumination is short compared with that required to reach a steady state.

(*c*) High sensibility of cells of high resistance.

(*d*) Decrease of inertia with increasing intensity of illumination, absorption coefficient, and "dark conductivity." This also explains variation of sensibility with temperature and other disturbing factors.

(*e*) Dependence of rate of recovery upon the same causes.

(*f*) Change in sensibility when cell is illuminated continuously with a beam of light for whose constituents k is nearly constant.

(*g*) Decrease in inertia when this beam is red, or infra-red.

(*h*) Possible explanation of "light-negative" selenium and anomalous effects.

In conclusion I beg leave to express my best thanks to Professor Ames and the entire staff of the physical laboratory of the Johns Hopkins University for interest taken in the work; also to Mr. S. M. Burka, who assisted me in the construction of apparatus and in taking readings. I feel that special mention should be made of Dr. Pfund, who suggested the work and spared no pains in aiding me in every possible way.

CHARACTERISTICS OF CRYSTAL RECTIFICATION.

BY ALAN E. FLOWERS.

IN an article published in the PHYSICAL REVIEW[1] some of the peculiarities of the uni-directional resistance between a conducting point and a rectifying crystal surface were described. Most of the measurements were made with direct current and the resistance showed a well-defined tendency to increase with time of current flow in the highly resisting direction and to decrease with time of current flow for the direction of easy current flow. Frequently, upon sudden reversal of current direction the initial resistance corresponded more nearly to the value just previous to reversal than to the final value for this direction of current. In most of the crystals examined some spots rectified well, and nearby portions of the surface rectified but little, if at all, or even gave rectification in the reverse direction. It was also found possible to produce rectifying spots on the surface of non-rectifying galena crystals by treating the surfaces with hot sulfur.

In view of these peculiarities it seemed desirable to subject crystals to very low and very high frequencies to see if time or energy were required to build up a resisting film upon change of current to the direction giving the higher resistance. Also it seemed desirable to determine the magnitude of the rectification at the high frequencies used in wireless telegraphy.

Two series of tests were carried out. One at Cornell University in December, 1910, was made possible by a grant from the Telluride Association, and another was carried out in the protective apparatus laboratory of the General Electric Company through the courtesy of Mr. E. E. F. Creighton, during the summer of 1912.

In the tests at Cornell University five different sources of supply were used. One of these was the 60-cycle lighting circuit. This was made the standard of comparison in every case. A double pole double throw switch was arranged so that the rectifier could be connected immediately either to this 60-cycle circuit or to the high frequency supply. The usual procedure was to measure the rectification on the 60-cycle circuit, then on a high frequency circuit, and again on the 60-cycle circuit as a check.

[1] 1909, Vol. XXIX., p. 445.

It is worth noting that the readings taken on the 60-cycle circuit in this way check with each other very well indeed, indicating a much greater constancy of rectification on alternating current than was to be expected from the variable values found when measuring the resistance with direct current. This method of checking both before and after the readings on high frequency eliminated chance effects such as, jarring, change of contact pressure, change of contact spot, etc. The contact point in these tests was a blunt ended piece of No. 13 B. & S. copper wire and the pressure on the point was about 250 grams. These values were such that considerable variations of either contact area or contact pressure would affect the rectification but slightly, if at all.

The effective value of the current was measured by means of a thermo-couple consisting of crossed wires of copper and constantan approximately 0.002 cm. in diameter. The current to be measured upon being passed through the copper-constantan crossover raised its temperature sufficiently to produce a thermal E.M.F. and a uni-directional current through a d'Arsonval galvanometer connected to the two ends of the crossed wires at right angles to the current path. A precaution to be observed in the use of this crossed-wire thermo-couple is to see that the crossed wires are well soldered together, otherwise the resistance of the contact causes current to flow directly through the galvanometer when calibrated with direct current or when being used for a partly rectified current. The deflections are then affected by the direction of the current through the couple and one may get a calibration curve that is nearer a straight line than a parabola. In taking measurements with this thermo-couple reversed readings were taken on the galvanometer to eliminate any slight error from this cause.

The average current was measured with a Weston permanent-magnet-type direct current mil-ammeter which gave full scale deflection for 20 milliamperes. For currents of 20 to 50 milliamperes this meter was shunted by non-inductive resistances.

Some of the results of these tests are presented in Table I.

A supply of approximately 2,000 cycles was obtained from an inductor alternator built by the Peerless Electric Company and belonging to the physics department. The wave shape given by this alternator is not known but is fairly smooth. The test results given in Table I. show a rectification ratio on 2,030 cycles very slightly poorer than on 60 cycles. The average difference from a number of such tests amounted to only 1 per cent. and could easily be attributed to wave shape. At the suggestion of Professor Frederick Bedell the effect of widely different wave shapes was tried making use of a complex wave consisting principally of

20-cycle and 60-cycle components which could be combined in different relative phase positions by varying the position of an induction motor rotor used as a transformer. The effective value being kept the same, the wave with the higher form factor should give the poorer rectification. This conclusion was confirmed by Tests Nos. 9 to 17 in Table I. The form factor for the wave given by rotor in position −20 was 1.154, while for the rotor in position 170 the form factor was 1.204. These values were calculated from the equations to the curve. I am indebted to Mr. Anderson, at that time a graduate student in Cornell University, for the use of this variable wave shape apparatus and for the equations to the curve. The difference in rectification was even greater than was to have been expected from the form factors. The effect of wave shape was even more marked on the poor rectifying spots where reverse rectification occurred.

In making the tests with very high frequencies use was made of a 500-volt direct current quenched spark oscillator. The arc played between electrodes lying in a powerful magnetic field and surrounded by

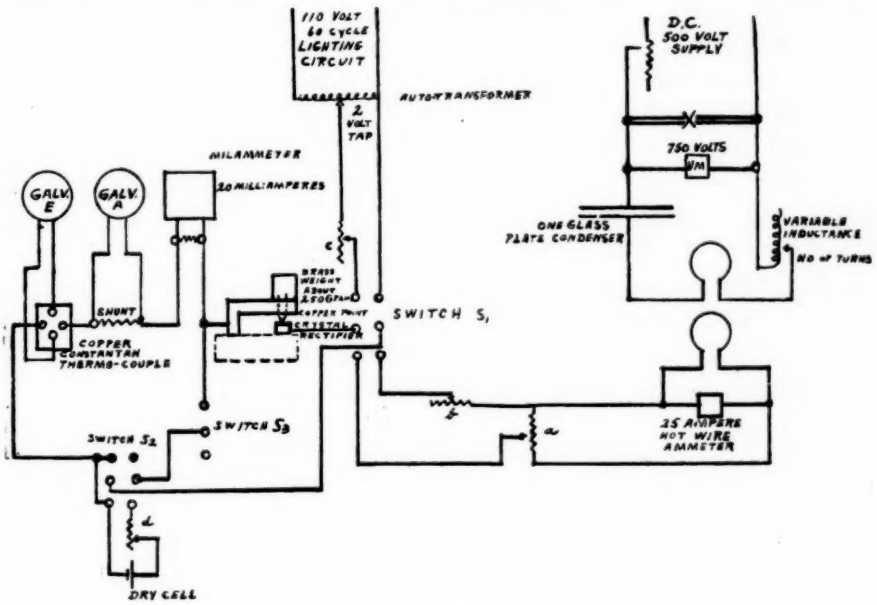

Fig. 1.

Diagram of Connections for Oscillatory Tests at Very High Frequencies.

an atmosphere of illuminating gas. This apparatus had been set up by Mr. F. H. Kroger, then of the electrical engineering department of Cornell University, who very kindly allowed its use for the purpose of carrying out these experiments. A diagram of the connections is shown in Fig. 1.

The arc was somewhat unsteady, consequently a number of readings were averaged in obtaining the results tabulated.

In every case the rectification was found to be better on the oscillating circuit than on the 60-cycle circuit. In several cases this effect was quite pronounced particularly when inductance was placed in series with the supply to the rectifier. The intermediate frequency of approximately 268,000 gave in all cases the best rectification. Tests 21 and 22 show that no disturbing effects were produced by the mere presence of the oscillating arc when the rectifier switch was closed on the 60-cycle circuit. The measuring circuit was inductively linked with the oscillating circuit and well insulated from it but it is possible that in some way leakage may have occurred, and caused part of the D.C. meter deflections. None of the attemps to detect such leakages resulted in discovering anything which caused a decrease in the readings of the meter which indicated effective values or an increase in the readings of the D.C. meter used to get the average or rectified current values.

The results of these tests indicate increased rather than decreased rectification for high frequency oscillating currents. It must be borne in mind, however, that these currents consist of more or less damped wave trains and that rectification varies with the magnitude of the current and the potential difference as will be shown later.

In the tests caried out in the protective apparatus laboratory of the General Electric Company a 60-cycle lighting circuit was again used as a standard to see that no permanent alteration had occurred in the crystal or contact. The high frequency supply was obtained from inductor type alternators giving frequencies up to 100,000 cycles per second for one machine and up to 200,000 cycles per second for the other machine. Some tests were also made using a spark discharge oscillating circuit inductively linked with the measuring circuit.

EFFECT OF CONTACT PRESSURE.

It was deemed wise to try the effects of considerable variation in contact pressure to settle definitely the question as to the possibility of variations caused by pressure changes being included in the other effects studied.

Variations of contact pressure on a blunt No. 13 B. & S. copper wire contact between 40 and 550 grams caused very small variations in the ratio of average to effective value of the current when using the 60-cycle supply. The rectification ratio, as just defined, varied between 57.3 and 59.6 per cent., and not more than half of this difference can be definitely ascribed to change of pressure. Another test made later at 100,000 cycles per second showed that the effects of very considerable

changes of pressure on the contact-point was negligible when the rectified current was as large as 20 milliamperes. Some observations with very small contact areas and very light pressures will be described later on.

Effect of Room Temperature.

The effect of temperature through a very wide range was described in the article already referred to (published in the Physical Review, November, 1909). The results showed a decrease of rectification with increased temperature; the rectification becoming unstable or disappearing at temperatures between 200 and 300 degrees centigrade. The change for room temperature variations was small and this was checked by a test made during the course of these experiments which showed a decrease from 58.9 per cent. to 57.9 per cent. when the temperature was raised approximately 10 degrees centigrade above the initial room temperature of 22 degrees. This difference is small enough to be negligible in comparison with the effects obtained in the course of this work.

Effect of Frequency.

The small effect of change of frequency is illustrated by the curves in Fig. 2. It is to be noted that a small but measurable increase in recti-

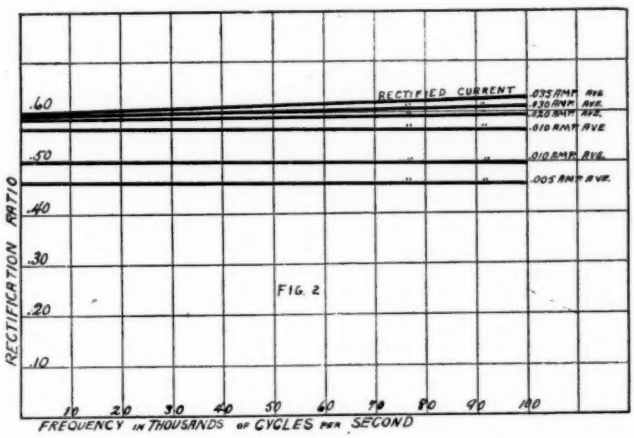

Fig. 2.

Effect of Frequency on Rectification Ratio for Various Rectified Currents.

fication occurred at the frequency of 100,000 cycles for the larger values of rectified current, but that for the smaller currents the rectification decreased slightly. Changes of wave shape may have had some effect, but such effect could not have been large for the alternator was run at low and high speeds for the readings, the current kept constant and hence

the reaction of the current on the field must have been almost exactly constant.

Another thing to be noted about the curves is that they show in general a better rectification for the larger currents. The rectification tended to increase with increase of current at 60 cycles per second and a similar effect was found at 100,000 cycles.

Some tests were made with a high frequency supply from an oscillating circuit. The oscillating circuit was excited by a Tesla coil, a sphere spark gap and a high voltage condenser. The oscillating circuit had a frequency of about 120,000 cycles per second as measured with a cymometer and was inductively linked with the rectifier and meters by a single turn air core coil.

The galena crystal which had been giving a rectification ratio of about 60 per cent. on the 60-cycle lighting supply or on the 100,000 cycle alternator gave only 3 per cent. to 5 per cent. rectification on the oscillating circuit. When reconnected later to the 60-cycle supply gave only 35 per cent. to 40 per cent. rectification. These results lead one to think that the high peak in the first wave of the oscillating wave train may have been sufficient to partially break down the rectifying film.

EFFECT OF CURRENT AND CURRENT DENSITY.

The noticeable decrease in rectification for small currents led to the attempt to measure the rectification ratio for exceedingly small currents. For these measurements the 60-cycle lighting circuit supply was employed and the value of the alternating curent measured by means of a separately excited dynamometer. The exciting current for the dynamometer was kept constant at 5 amperes and its phase adjusted by means of a phase shifting transformer to give the maximum deflection of the dynamometer. Trial showed that the position of the phase shifter for maximum deflection on the dynamometer was the same for either small or large currents. An instrument of this type really measures the average value of the current without regard to the direction of current flow; consequently the limit of the rectification ratio, as employed here, would be 100 per cent. for complete rectification of a sine wave, while the limit for a sine wave whose effective value was measured would be 91 per cent. This drawback would not greatly affect different readings all taken on the same dynamometer and under the same conditions.

The curve given in Fig. 3 shows that for currents of the order of 1 to 2 microamperes of rectified current the rectification ratio is less than 10 per cent. The same conditions (No. 13 B. & S. blunt copper wire point

and 276 grams contact pressure) gave rectification ratios of over 80 per cent. for rectified currents of 500 microamperes. This is shown in

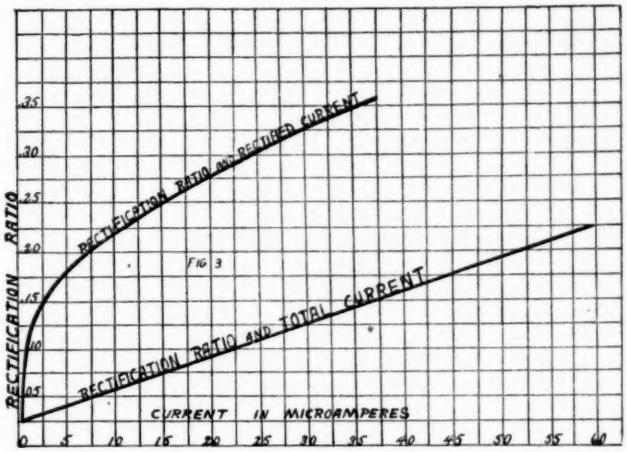

Fig. 3.

Relation of Rectification Ratio and Current at 60 Cycles for Very Small Currents. No. 13 blunt copper wire contact. 276 grams contact pressure. Total current measured with separately excited dynamometer.

Fig. 4 where the results for the whole range of currents are shown in one curve. The rectification ratios in the tests shown in Figs. 3 and 4

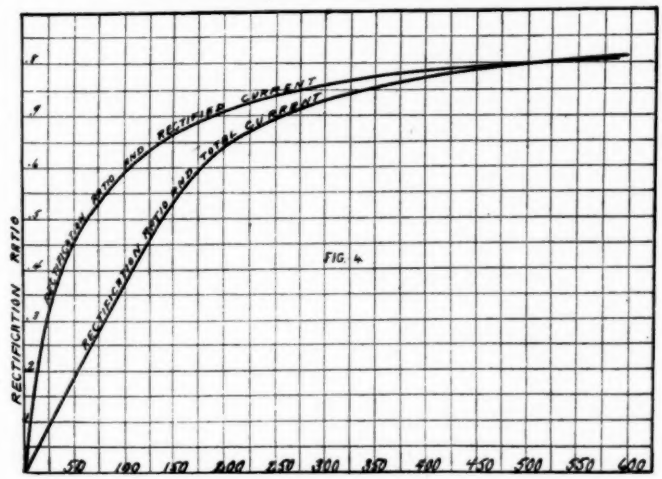

Fig. 4.

Relation of Rectification Ratio and Current at 60 Cycles. No. 13 blunt copper wire contact, 276 grams contact pressure. Total current measured with separately excited dynamometer.

vary as the *square* of the rectified current and as the *first power* of the whole current throughout a considerable range.

EFFECT OF CONTACT PRESSURE ON RECTIFACTION OF VERY SMALL CURRENTS.

The preceding test which showed that the rectification ratio was very low for small currents suggested that the current density must be a large factor, consequently other tests were made with normal and reduced pressures on the No. 13 B. & S. blunt copper wire point. The tests already described using larger currents had shown but little influence of pressure between 38 and 276 grams. For small currents, however, it was found in this test that quite considerable differences in rectification existed for small rectified currents. The lighter pressure on the point gave an appreciably better rectification, as is shown in Fig. 5.

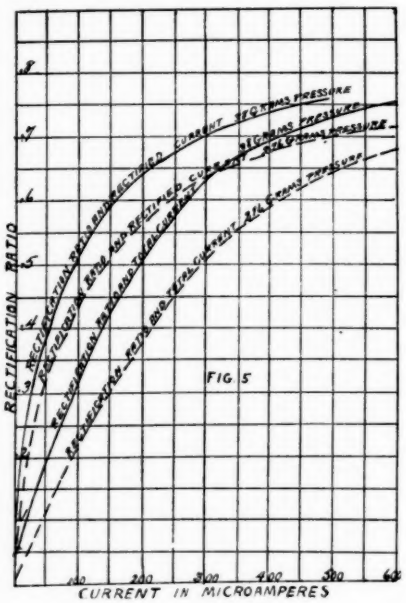

Fig. 5.

Effect of Contact Pressure and Current on Rectification Ratio for Small Currents. 60-cycle supply No. 13 B. & S. blunt copper wire contact. Total current measured with separately excited dynamometer.

EFFECT OF SIZE OF CONTACT POINT.

In order to still further investigate the question of current density tests were made with very fine wires giving small contact areas and with a contact made by a drop of mercury about 3 mm. in diameter. The contact area must bear some relation to the cross section of the wires except possibly in the case of the No. 13 copper wire which was too large to touch over its whole surface area.

The results tend in general to show that, for very small currents at least, the reduction in size of contact points improves the rectification ratio very markedly. It was noted, however, that much larger voltages had to be employed to get the same current.

Fig. 6 shows the results for a 7 mil (0.0178 cm.) copper wire. The

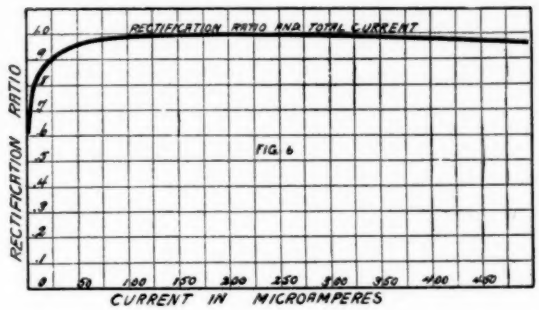

Fig. 6.

Relation of Rectification Ratio and Current at 60 Cycles for a Small Copper Wire Point, .0178 cm. in Diameter. Total current measured with a separately excited dynamometer.

section area of this wire was 2.49×10^{-4} cm., and the curve shows the fairly large rectification ratio of 63 per cent. for very minute rectified currents, *i. e.*, values of 2 to 3 microamperes. For larger rectified currents the rectification ratio was even higher. Even for 0.7 of a microampere this small copper wire gave a rectification ratio of 35 per cent. For currents over 50 microamperes the readings taken gave rectification ratios that indicated practically complete rectification.

A still smaller silver wire 0.0025 cm. in diameter, section area 4.9×10^{-6} sq. cm. while requiring a still higher voltage to give readable currents gave rectification ratios of the very small currents not quite so good as in the preceding test. Another peculiar action which occurred with this extremely small silver wire point was *reverse* rectification on the first application of voltage followed by a sudden decrease in the value of the current, then a change of direction of rectified current to the direction usually found accompanied by very good rectification. On decreasing the supply voltage and thus reducing the current there was a decided tendency for reversal of rectification to proceed of itself as soon as the total current lowered to a value less than 75 to 100 microamperes. Reversed rectification ratios of 35.5 per cent. or more were obtained in this way. In one case 65 per cent. reversed rectification ratio was obtained with 7 microamperes total current. This was obtained, however, by using the smallest obtainable value for the supply voltage.

The current was not stable when using this 0.0025 cm. silver wire and when the results were plotted as in Fig. 7 the curve brings out only the marked tendency to drift towards reverse rectification for low voltages and small total currents.

A check test with a 0.005 cm. copper wire gave results similar to those of the 0.0178 copper wire already described and no reversal of rectification such as was observed with the 0.0025 cm. silver wire.

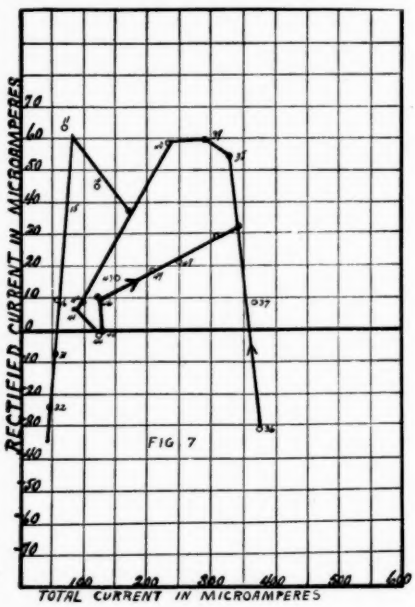

Fig. 7.

Rectification with an Extremely Small Silver Wire Point, .0025 cm. in Diameter. 60-cycle supply. Total current measured with a separately excited dynamometer.

A check test with the large blunt copper point made of No. 13 B. & S. wire gave again results similar to those obtained in the earlier tests under the same conditions. The effect of very large size contact areas giving a very low current density was investigated by the use of a drop of mercury about 3 mm. in diameter, having thus a contact area of 0.07 sq. cm. The results are plotted in Fig. 8.

The highest rectification ratio obtainable with this large contact area was about 10 per cent. and even this required a total current of 60 milliamperes. For currents between 150 and 2,500 microamperes the rectification ratio was less than .1 of 1 per cent. For total currents less than 150 microamperes it was found that the crystal alone gave a direct E.M.F. that affected the galvanometer, giving from 12 to 14 mm.

deflection corresponding to a direct current of 0.12 to 0.14 microampere, so that the apparent rectification ratios rose again to something over 1 per cent. for total currents less than 15 microamperes.

This test gave also an opportunity to compare the readings of the dynamometer with those obtained by the thermo-couple. When in series the current as calculated was 0.00298 ampere for the heated thermo-couple and 0.002455 from the dynamometer reading. The values as

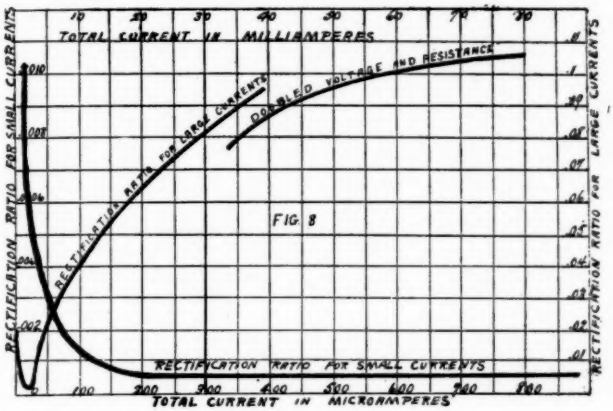
TOTAL CURRENT IN MILLIAMPERES
RECTIFICATION RATIO FOR SMALL CURRENTS
RECTIFICATION RATIO FOR LARGE CURRENTS
DOUBLED VOLTAGE AND RESISTANCE
FIG. 8
RECTIFICATION RATIO FOR SMALL CURRENTS
RECTIFICATION RATIO FOR LARGE CURRENTS
TOTAL CURRENT IN MICROAMPERES

Fig. 8.

Effect of Current on Rectification for Very Large Contact Area. 3 mm. mercury drop contact. Total current measured with a separately excited dynamometer.

read on the dynamometer are therefore smaller than the effective value of the current, and, according to this one check, even somewhat smaller than the ratio of average to effective value of a sine wave. This would, however, tend to make the real rectification ratios *higher* for all the small currents where such low values were found. The validity of this conclusion in regard to the method of measuring the total current is further checked by the higher rectification ratios obtained for currents greater than half a milliampere.

Effect of Frequency and Low Current Density.

If high frequency currents were less well rectified than currents of low frequency such an effect should be most marked with the combination of large contact area, small current, and high frequency. It has already been shown that small currents of normal frequency are but imperfectly rectified when the contact area is large.

Fig. 9 shows the results of tests at different frequencies using the 60-cycle lighting circuit and the high frequency alternator, for several values of rectified current. The rectified current was kept constant and

the frequency changed. The effective current was measured in this case with the crossed-wire thermo-couple. These results show, as before, small rectification ratios particularly for the small currents; but the effect of increasing the frequency to 100,000 cycles per second is negligible even for this large contact area and extremely small current density.

The rectification curve for the highest frequency obtainable from the 100,000 cycle alternator lies only a very little below that for the lowest frequency obtainable from the same machine. Both these curves show, however, higher rectification than on the 60-cycle circuit. As far as possible the circuit conditions were kept the same, particularly with regard to resistance, the voltage control being obtained by the use of step-up or

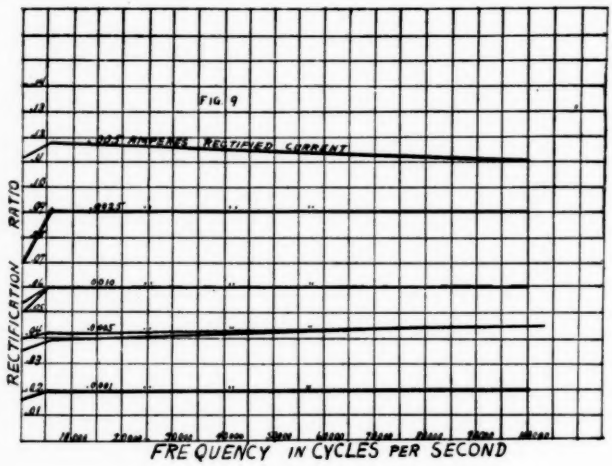

Fig. 9.

Effect of Frequency on Rectification for Small Current and Large Current Area. 3 mm. mercury drop contact.

step-down transformers, moderate changes of field current, and finally by shunt and series rheostats for fine adjustments.

It is also fairly evident from the trend of these curves that larger currents (involving higher voltage) would give very much better rectification. This was proven by later tests which showed rectification ratios of 30 per cent. to 40 per cent. for 2 to 2.5 volts on the crystal rectifier and 1/2 to 3/4 ampere total current. This result is stated here in order to show that the low rectification ratios found with the large contact areas (7 sq. mm.) are due to the low current density and not to accidently touching upon a non-rectifying spot. There is always considerable likelihood with the crystal rectifiers of getting on non-rectifying spots. This particular crystal had been found to have, about 18 months previous to these tests, on its top surface, *one part* which would give

reversed rectification. The whole surface at the period of these tests gave rectification in the usual direction. This change is particularly interesting in view of the results obtained by R. H. Goddard and published in the PHYSICAL REVIEW for Feb., 1912, Vol. 34, p. 149, showing the absence of rectification on surfaces freshly broken in a vacuum where they would be quite free from oxidizing influences.

VOLT-AMPERE CHARACTERISTICS.

The rectification of small currents is better with small contact areas, but this improvement is obtained at the expense of higher applied voltages. In view of this fact further tests were made in which the applied voltage was kept constant. Hot wire voltmeters and ammeters were used in these tests to measure the effective values of voltage and current. The rectified current was measured by a permanent-magnet moving-coil-type meter.

The volt-ampere characteristic when using the blunt No. 13 B. & S. copper point on 60 cycles per second gave a nearly linear increase of rectified current with increase of voltage, but a more rapid increase of total current so that the rectification ratio decreased markedly as the voltage across the rectifier was raised from 1 to 3 volts.

The volt-ampere and rectification characteristics with the very large contact area of 7 sq. mm. obtained when using the mercury drop for a contact gave the fairly high rectification ratios of 30 to 45 per cent. when the total current reached values of .3 to .4 ampere. The better rectification occurred at the high frequency of 180,000 cycles. Possibly the skin effect at this frequency would give increased current density at the outer edges of the drop and so produce a better rectification.

The nominal current density for maximum rectification ratio of 35 to 45 per cent. varies between 5 and 6½ amperes per sq. cm. with this large contact of 7 sq. mm. irrespective of frequency.

A comparison of the tests at 60 cycles per second show nominal current densities for maximum rectification ratio as follows, the maximum rectification ratio corresponding in all case to nearly complete rectification.

Point.	Nominal Current Density for Maximum Rectification.
No. 13 B. & S. copper wire point	7 –
.0178 copper wire point	½ to 5
.005 copper wire point	6
.0025 silver wire point	16

The currents range from 50×10^{-6} amp. for the smallest wires to nearly half an ampere, a range of variation of 1 to 10,000 and the areas

vary through a similar range, but even these approximate calculations give only a moderate change of optimum current density.

It is hoped that this work may be followed by other more precise measurements which will make it possible to settle upon definite quantitative values for optimum current density.

If the contact area be very large, the optimum current density may not be reached even when the voltage approaches the critical value, consequently the rectification ratio may be limited to low values.

EFFECT OF FREQUENCY ON RECTIFICATION AT CONSTANT VOLTAGE.

The first tests were made with a No. 13 B. & S. blunt copper wire point under 276 grams pressure resting on the same crystal that had been used in the preceding tests. The high frequency supply was taken from the inductor type alternator and the low frequency standard supply from the 60-cycle lighting circuit. Fig. 10 shows that for these conditions

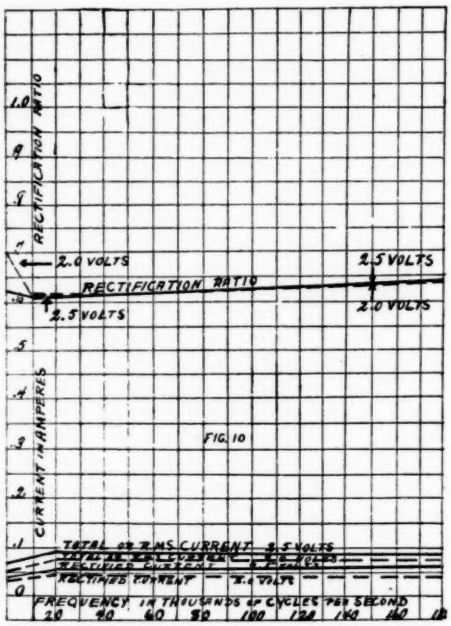

Fig. 10.

Effect of Frequency on Rectification at Constant Voltage. No. 13 blunt copper wire contact, 276 grams contact pressure.

the rectification ratio, the total current, and the rectified current, increaes slightly at the highest frequencies. The best rectification as given in Fig. 10 is 65 per cent. at 180,000 cycles per second.

The resistance of the hot-wire mil-ammeter was rather large (about

16 ohms) and the effect of this resistance in decreasing the rectification was quite marked.

The results at high and low frequency were very similar, as might be expected from the results already given in Fig. 2 but both rectified and total current were somethat greater than at 60 cycles. The difference was greatest at the higher voltages. At 2.5 volts the current values at 180,000 cycles were about 30 per cent. higher than at 60 cycles but the rectification ratio was very nearly the same; 61 per cent. at 60 cycles and 63 per cent. at 180,000 cycles. The numerical values for current and rectification ratio obtained with these hot wire meters should not be given too much weight, because the calibration corrections as given for these meters are rather large and the ammeter measured also, necessarily, the current required by the voltmeter for its deflection and this correction to the ammeter readings had to be applied in all these tests. The voltmeter

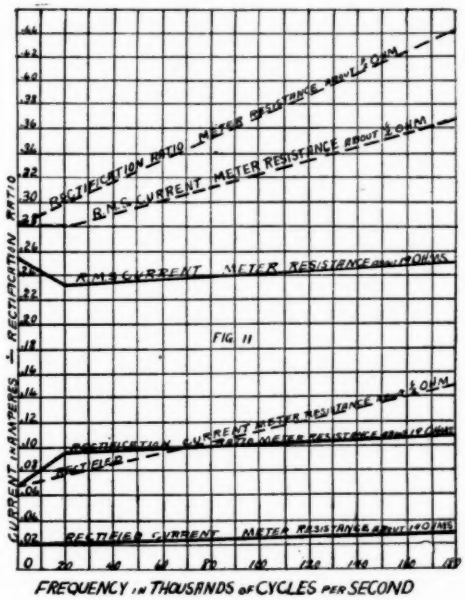
RECTIFICATION RATIO
R.M.S. CURRENT METER RESISTANCE ABOUT ½ OHM
RECTIFIED
RECTIFIER CURRENT METER RESISTANCE ABOUT 100 OHMS
CURRENT IN AMPERES & RECTIFICATION RATIO
FREQUENCY IN THOUSANDS OF CYCLES PER SECOND

Fig. 11.

Effect of Frequency and Meter Resistance with Large Contact Area and 1.8 Volts on Rectifier. 3 mm. mercury drop contact. Meter resistance 19 ohms and ½ ohm.

was connected directly across the rectifier thus excluding meter drops. These drawbacks do not affect the value of the *comparisions* on low and high frequency.

In order to get the combined effect of low current density and high frequency other tests were made at constant voltage using the same crystal but with the contact consisting of a mercury drop about 3 mm.

in diameter resting on the top surface of the crystal. Part of the results in terms of current and rectification ratio are plotted in Fig. 11 (for 1.3 volts across rectifier) to show the effect of frequency at constant voltage.

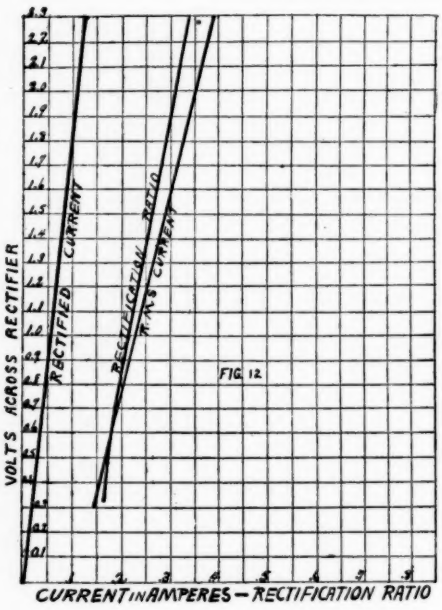

Fig. 12.

Low Frequency Volt-Ampere and Rectification Characteristic with Large Contact Area. 3 mm. mercury drop contact. 60-cycle supply. Meter resistance ½ ohm.

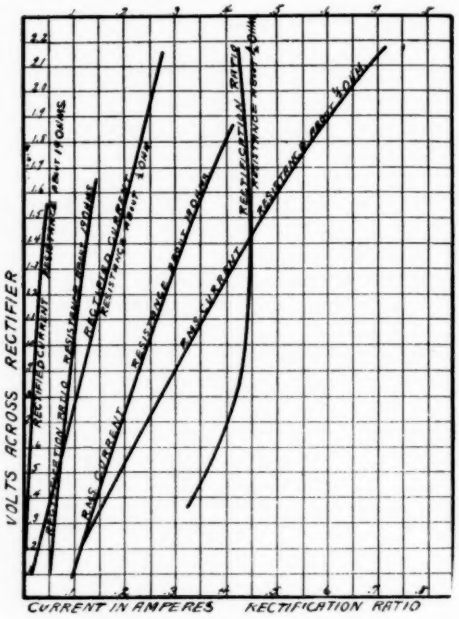

Fig. 13.

High Frequency Volt-Ampere and Rectification Characteristic with Large Contact Area, at 180,000 Cycles per Second. 3 mm. mercury drop contact.

The effect of reducing the circuit resistance by making use of low resistance meters is very marked, particularly on the rectification ratios. The shorting of two meters, one the hot-wire mil-ammeter (0.25 ampere full scale deflection) having 16 ohms resistance and the D.C. mil-ammeter (0.20 ampere full scale deflection) having 2.5 ohms resistance thus reduced the resistance of the circuit 18.5 ohms; that is, from about 19 ohms to about 0.5 ohm. This reduction in resistance made a moderate increase in the total current but a very great increase in the rectified current and consequently in the rectification ratio. Apparently the difference is not due to the elimination of the inductance of the D.C. meter the resistance of which was small (2.5 ohms), but is largely due to the elimination of the reistance of the small scale hot-wire mil-ammeter which had a resistance of 16 ohms as determined by test during the course of these experiments. This conclusion is based upon the values obtained

TABLE I.

Effect of Frequency and Wave Shape on Rectification.

	Date of Test.	Rectifier.	Frequency Cycles per Second.	Current. Effective Value Milli-amp.	Current. Average Value for Current Milli-amps.	Rectification Ratio.
1.	Dec. 21, 1910	M	60	8 to 38		.544
		P	60	21.9		.568
2.	Dec. 28, 1910	P	60	41.5	25.75	.619
		P_1	2,030	40.4	24.90	.616
3.	Dec. 29, 1910	P_1	60	34.35	19.6	.571
4.			2,020	34.35	19.47	.567
5.	Dec. 29, 1910	M	60	21.4	13.7	.640
6.			2,150	21.4	13.4	.626
	Set Contact on Area for Reversed Rectification.					
7.	Dec. 29, 1910	M_1	60	45.4	1.5	.0331
8.			2,150	43.1	.45	.0104
	Effect of Wave Shape.					
9.	Dec. 29, 1910	P_1	60	28.6	18.4	.633 standard
10.			20+60	30.28	18.7	.618 flat-topped wave
11.			20+60	30.28	14.5	.479 peaked wave
	Effect of Wave Shape Using Spot Having Reversed Rectification.					
12.	Dec. 29, 1910	M	60	47.5	.8 (Unsteady)	.01685
13.			20+60	46.6	.4 (Unsteady)	.00858 flat-topped wave
14.			20+60	46.5	.25 (Unsteady)	.00538 peaked wave
	Effect of Wave Shape with Point Reset for Usual Direction of Rectification.					
15.	Dec. 29, 1910	M	60	28.35	18.55	.654 standard
16.			20+60	8.20	5.35	.652 flat-topped wave
17			20+60	9.73	5.00	.513 peaked wave
	High Frequency Supply from Quenched Spark Oscillating Circuit.					
21.	Dec. 30, 1910	M	60	59.4	35.23	.5935
22.			60	58.9	34.97	.5955
23.			268,000	36.95	28.18	.763
24.			60	56.	33.40	.597
24′.			60	36.9	21.60	.586
25.	Dec. 31, 1910	M	60	49.02	29.56	.603
26.			678,000	52.18	32.70	.626
27.			268,000	37.50	28.60	.7688
28.			60	50.81	30.66	.603
29.			60	30.62	18.48	.604
30.			268,000	25.52	18.70	.7326
31.			678,000	26.31	18.56	.7053
32.			678,000	32.56	20.42	.638
33.			678,000	54.13	32.55	.605
34.			60	29.95	18.24	.6088

TABLE I.—*Continued.*

High Frequency Supply from Quenched Spark Oscillating Circuit.

	Date of Test.	Rectifier.	Frequency Cycles per Second.	Current. Effective Value Milli-amp.	Current. Average Value for Current Milli-amps.	Rectification Ratio.
35.	Dec. 31, 1910.	*M*	268,000	25.02	18.45	.7375
36.			678,000	27.27	17.98	.661
	Air Core Induction Coil in Series with Supply to Rectifier.					
37.			60	29.79	18.17	.6103
38.	Dec. 31, 1910	*M*	268,000	17.68	17.44	.986
39.			678,000	14.09	9.46	.6744

when first one and then the other of these two meters was short-circuited. In this connection it should be stated that the hot-wire voltmeter was connected directly across the terminals of the rectifier so that none of these changes of ammeter resistance could affect the accuracy of the values taken for the potential difference across the rectifier. In all cases the A.C. ammeter readings have had subtracted from them the values corresponding to the current through the voltmeter. The values for these corrections to the ammeter readings were obtained by a separate experiment. The magnitude of these corrections is well brought out by the data recorded in Tables II. and III.

The results in Table II. and in Fig. 10 have been corrected for voltmeter current but the values *given* for the hot-wire A.C. ammeter calibration errors have not been used in calculating the results. In Table III. and in Figs. 11, 12, and 13 the effect of the voltmeter current and also the calibration errors of the ammeters have been allowed for. There is some doubt as to the values that should be used for the calibration corrections. The omission of the calibration corrections gives somewhat larger values for the effective current and lower values for the rectification ratio, particularly for the smaller currents.

SUMMARY AND CONCLUSIONS.

1. The rectification at high frequency tends to be greater than at low frequency with the larger currents, and but very little different for small currents.

2. For very small currents the rectification tends to disappear, particularly for large contact areas and low current densities.

Table II.

Volt-ampere. Rectification Characteristics at Low and High Frequency.

Galena Crystal M, No. 13 B. & S. with Blunt Copper Wire Point and a Contact Pressure of 276 Grams.

Rectified or Direct Current.		Total Current.		Voltage on Rectifier.	Voltmeter Current, Amp.	Net Current through Rectifier, Amp.	Rectification Ratio.
No. 3,815. .020 Sc., 2.5 Ohm, Amp.	No. 263, .5 Sc., .08 Ohm, Amp.	No. 5.535, 2 Scale, .26 Ohm, Rdg. Amp.	No. 47,201, .25 Sc., 16 Ohm, Rdg. Amp.	No. 47,203 5 Scale, Volts.			
			60-cycle Lighting Circuit Supply, Meter 3815.				
.0073	.0075	?	.032	.5	.015	.017	.430
.0127	.013	.1 est.	.054	1.0	.031	.023	.550
.0205	.0205	.1 est.	.085	1.5	.0475	.0375	.547
			Meter 263.				
Shorted	.024	.1 est.	.090	1.5	.0475	.0425	.565
	.035	.2 est.	.128	2.0	.0625	.0655	.534
	.045	.2	.161	2.5	.080	.0810	.555
	.036	?	.130	2.0	.0625	.0675	.533
	.025	?	.091	1.5	.0475	.0435	.575
	.0165	?	.062	1.0	.0310	.0310	.533
	.036		Shorted	1.0	.0310		
	.059			1.5	.0475		
	.085			2.0	.0625		
	.118	.28 est.		2.5	.080		
.0193	.019	?		.5	.016		
			180,000-cycle Supply from Inductor Alternator.				
.0122	.012		.044	.5	.015	.029	.421
.0189	.018		.064	1.0	.031	.033	.572
Shorted	.019		.063	1.0	.031	.032	.594
	.024		.078	1.2	.0355	.0425	.565
	.031		.099	1.5	.0475	.0515	.602
	.041		.129	1.8	.056	.073	.562
	.046		.143	2.0	.0625	.0805	.572
	.052		.161	2.2	.069	.092	.565
	.057		.175	2.4	.076	.099	.576
	.060		.180	2.5	.080	.100	.60
	.053		.165	2.2	.068	.097	.547
	.047		.146	2.0	.0625	.0835	.573
	.033		.106	1.5	.0475	.0585	.564
	.021		.070	1.0	.031	.049	.428
			20,000-cycle Supply from Inductor Alternator.				
.012	.012		.044	.6	.018	.026	.462
.0163	.016		.060	1.0	.031	.029	.562
Shorted	.018		.067	1.0	.031	.036	.500
	.028		.099	1.5	.0475	.0515	.544
	.036		.125	1.8	.056	.069	.522
	.043		.144	2.0	.0625	.0815	.527
	.050		.165	2.3	.0725	.0925	.541
	.0545		.179	2.5	.080	.099	.55
	.043		.145	2.0	.0625	.0825	.521
	.030		.103	1.5	.0475	.0555	.540
	.020		.070	1.0	.031	.039	.645?

TABLE II.—*Continued.*

Check on 60-cycle Lighting Circuit.

Rectified or Direct Current.		Total Current.		Voltage on Rectifier.	Voltmeter Current, Amp.	Net Current through Rectifier, Amp.	Rectification Ratio.
No. 3,815, .020 Sc., 2.5 Ohm, Amp.	No. 263, .5 Sc., .08 Ohm, Amp.	No. 5,535, 2 Scale, .26 Ohm, Rdg Amp.	No. 47,201, .25 Sc., 16 Ohm, Rdg. Amp.	No. 47,203, 5 Scale, Volts.			
10	.010		.040	.5	.015	.025	.40
15	.015		.056	1.0	.031	.025	.60
Shorted	.016		.060	1.0	.031	.029	.552
	.026		.093	1.5	.0475	.0455	.572
	.037		.132	2.0	.0625	.0695	.532
	.046		.165	2.5	.080	.085	.541
	.037		.135	2.0	.0625	.0705	.525
	.026		.095	1.5	.0475	.0475	.548
	.021		.063	1.0	.031	.032	.656
	.0105		.044	.5	.013	.031	.339
	.021		Shorted	.5	.013		
	.037			1.0	.031		
	.060			1.5	.0475		
	.093			2.0	.0625		
	.120			2.5	.080		
	.099			2.0	.0625		
	.041			1.0	.031		

3. The rectification ratio for small currents is nearly proportional to the square of the rectified current and nearly proportional to the first power of the total or R.M.S. current.

4. Even very large contact areas will rectify well with large currents.

5. The rectification *ratio* for very small currents may be improved by the use of very small contact points but a much larger potential is required to get the same amount of current.

6. The current density must be equal to or greater than a given minimum value for good rectification.

7. Resistance in series with the galena crystal rectifier greatly decreases the rectification ratio even for the same potential difference on the terminals of the rectifier.

OHIO STATE UNIVERSITY,
November, 1913.

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TABLE III.

Volt-ampere and Rectification Characteristic at Low and High Frequency.
Galena Crystal M. 60-cycle Supply. 3 mm. Mercury Contact.

Direct or Rectified Current.	Total Value or Effective Value of Current.					Potential on Rectifier, No. 47,203, 5 Scale, Volts.	Voltmeter Current, Amp.	Net Current through Rectifier.	Rectification Ratio.
No. 3,815 (Weston), .020 Scale, 2.3 Ohms, Amp.	No. 263 .5 Sc., .2 Ohm.	No. 5,535, 2 Scale, .26 Ohm.		No. 47,201, .25 Scale, 16 Ohm.					
	Amp. Rdg.	Amp. Rdg.	Amp. Value.	Amp. Rdg.	Amp. Value.				
1	2	3	4	5	6	7	8	9=4 or 6-8	10
.015	.015	.250	.22	.208	.223	1.0	.030	.220	.068
.0196	.020	.300	.27	.239	.260	1.3	.040	.199	.100
Shorted	.031	.220	.190	Shorted		.5	.015	.175	.177
this meter	.050	.280	.250	this meter		1.0	.030	.220	.227
	.080	.410	.360			1.5	.046	.314	.254
	.113	.510	.460			2.0	.062	.400	.283
	.135	.650	.610			2.5	.079	.530	.255
	.113	.450	.390			2.0	.062	.330	.347
	.080	.400	.340			1.5	.046	.294	.272
	.052	.320	.280			1.0	.030	.250	.208
20,000 Cycle. R = 19.16 Ohms.									
.0021	.002			.067	.055	.1	.003	.052	.0403
.0033	.003	?		.084	.075	.15	.007	.068	.0485
.0074	.0075	.1		.132	.129	.3	.009	.120	.0616
.00955	.0095	.1		.161	.163	.5	.015	.148	.0645
.01640	.0170	.23		.213	.228	1.0	.030	.198	.0828
.01780	.0180	.24	.21	.217	.234	1.1	.033	.201	.0886
.02000	.0200	.26	.23	.233	.259	1.2	.037	.222	.0901
R = 16.66. Voltage rose because D.C. meter was short-circuited.									
Shorted	.0250	.30	.27	.248	.283	1.38	.042	.241	.1037
	.0190	.26	.23	.228	.251	1.20	.037	.214	.0889
Shorted this meter, making the resistance of the meters .66 ohm. This reduction of resistance increased the meter readings until the supply was readjusted.									
	.127	.47	.41			1.73	.053	.36	.353
	.043	.22	.19			.5	.015	.175	.246
	.063	.29	.26			1.0	.030	.23	.274
	.079	.33	.29			1.2	.037	.25	.316
	.093	.40	.34			1.38	.042	.30	.310
	.098	.42	.37			1.50	.046	.32	.306
	.123	.48	.43			1.73	.053	.38	.324
	.113	.48	.43			1.90	.059	.37	.307
	Tapped lightly								
	.127	.49	.44			1.9	.059	.38	.334
	.130	.50	.45			1.73	.053	.40	.325

TABLE III.—*Continued.*

20,000 Cycle. R = 19.16 Ohms.

Direct or Rectified Current.	Total or Effective Value of Current.								
No. 3,815 (Weston), .020 Scale, 2.5 Ohms, Amp.	No. 263, .5 Sc., .2 Ohm.	No. 5,535, 2 Scale, .26 Ohm.		No. 47,201, .25 Scale, 16 Ohms.		Potential on Rectifier, No. 47,203, 5 Scale, Volts.	Voltmeter Current, Amp.	Net Current through Rectifier.	Rectification Ratio.
	Amp. Rdg.	Amp. Rdg.	Amp. Value.	Amp. Rdg.	Amp. Value.				
1	2	3	4	5	6	7	8	9=4 or 6-8	10
	.143	.55	.51			1.90	.059	.45	.318
	.151	.58	.53			2.0	.062	.47	.321
	.108	.45	.39			1.5	.046	.34	.318
	.069	.33	.29			1.0	.030	.26	.265
	.042	.23	.20			.5	.015	.18	.233
180,000 Cycles.									
.0058	.006			.117	.112	.2	.006	.106	.0557
.0116	.0115	.180	.15	.161	.163	.5	.015	.148	.0784
.0195	.0195	.25	.22	.223	.244	1.0	.030	.214	.0911
Shorted this	.0275	.30	.27	.250	.287	1.24	.038	.249	.1104
meter	.0150	.20	.17	.183	.189	.50	.015	.174	.0862
	.022	.27	.24	.223	.239	1.0	.030	.209	.1052
	.026	.28	.25	.244	.277	1.2	.037	.240	.1083
	.184	.50	.45	Shorted this meter		1.45	.045	.410	.445
	.081	.26	.23			.6	.018	.21	.385
	.125	.36	.31			1.0	.030	.28	.449
	.137	.40	.34			1.1	.033	.31	.442
	.149	.43	.38			1.2	.037	.34	.438
	.078	.25	.22			.6	.018	.20	.390
	.124	.37	.32			1.0	.030	.29	.428
	.135	.40	.34			1.1	.033	.31	.436
	.147	.43	.38			1.2	.037	.34	.432
	.178	.49	.44			1.4	.043	.40	.445
	.204	.55	.51			1.6	.049	.46	.443
	.234	.62	.57			1.8	.056	.514	.455
	.257	.69	.67			2.0	.062	.61	.422
	.275	.75	.72			2.2	.068	.65	.423
	.303	.87	.86			2.5	.079	.78	.389
	.258	.71	.67			2.0	.062	.61	.423
	.208	.59	.54			1.6	.049	.49	.425
	.185	.51	.46			1.4	.043	.41	.452
	.157	.45	.39			1.2	.037	.35	.448
	.129	.40	.34			1.0	.030	.31	.416
.0190	.019	.25	.22	.220	.239	1.0	.030	.209	.091
.0121	.012	.20	.17	.176	.181	.5	.015	.166	.073
.0061	.006	.1 Est.		.121	.116	.2	.006	.110	.055

SOME OBSERVATIONS ON SELECTIVE REFLECTION FROM SOLUTIONS IN THE INFRA-RED.

By A. K. Ångström.

DRUDE'S[1] theoretical considerations led him to regard the ultra-violet absorption lines as due to the vibration of particles of the size of an electron, while the particles giving rise to the infra-red absorption bands have a mass of the order of magnitude of the molecule.

In accord with the theory the investigations of Pfund,[2] Morse,[3] Langford[4] and others, and specially the comprehensive works by Coblentz[5] indicate that the mechanism giving rise to strong maxima of reflection in the infra-red spectrum, in the case of salts, is localized within the acid radical. Salts of the same acid have characteristic reflection-maxima, whose positions are more or less independent of the positive radical. Further investigations have shown that a change of the positive radical generally gives rise to a slight change in the period of the vibration, in such way that an increase in the molecular weight of the base causes a shift of the absorption (reflection) band to longer wave-lengths. Several relations have been tried in order to express this shift as a function of the molecular weight of the constituents; none of them seems to be of general applicability.

Under conditions, where the absorption coefficient is unusually large, as is the case for most crystals at several points in the infra-red spectrum, and for water in the infra-red, the *reflecting power* gives an important means of detecting the position and slight variations in the absorption bands, a method; first used in the classical investigations of Rubens and Nichols.

In the present note, I will describe some measurements with aid of the spectrometer and the Nichols' radiometer, where the selective reflection properties of water have been used in order to detect slight variations in the free period of vibration, when different compounds are dissolved

[1] Annalen der Physik, *14*, 677, 1904.

[2] Astrophysical Journal, XXIV., 19, 1906.

[3] Physical Review, *25*, 500, 1907.

[4] Physical Review, *33*, 137, 1911.

[5] Coblentz, Investigations of Infra red Spectra. Publ. by the Carnegie Inst. of Washington. Parts IV. and V.

in the water. These observations are closely connected with the problem of the rôle of the solvent in solutions, a problem that has been extensively studied by H. C. Jones and his collaborators at Johns Hopkins University. The observations of Guy, Shaeffer and Jones[1] indicate that under special conditions there occurs a shift of the spectral bands of the solvent to the long wave-lengths with an increase in the concentration of the dissolved substance. They observed further that the absorption power of the solution was sometimes considerably less than the absorbing power of the water present in the solution. This seems to be the case when this dissolved substance is a strongly hydrated salt, and the view held by the authors is that this shift and this change in the absorption power is due to a chemical reaction taking place in the solution, a part of the water combining with the dissolved substance to form hydrates. Such a hypothesis will evidently account for the observed facts. It has, however, since been pointed out by G. H. Livens,[2] that the results obtained by Guy, Shaeffer and Jones can be derived from the dispersion and absorption theory in the form given by Lorentz without any hypothesis in regard to intramolecular changes taking place in the solution. The point brought forward by Livens seems well worth the attention of the upholders of the solvate theory. From the purely physical point of view, it seems however difficult to account for the fact that the observed shift only occurs in measurable degree in the case when the dissolved substance is a strongly hydrated salt.

Before the results of Jones and the theoretical considerations of Livens were communicated, I had begun a study of the influence of the dissolved substance upon the strongly marked water band at 3 μ, that gives rise to a very sharp and definite reflection maximum at 3.18 μ. The absorption of water in this region is such that a layer of only 3 μ thickness absorbs almost totally, and it is therefore preferable to use the reflection properties as an indicator of the selective conditions.

As the study has brought forward some facts that require to be taken into consideration in forming a view upon the question, some preliminary results are here published.

Instruments.

The general arrangement of the apparatus is shown in Fig. 1. A reflection spectrometer with mirrors of 6 cm. aperture and 54 cm. focal length was used. By aid of the Wadsworth mirror prism arrangement, the spectrometer arms could be kept fixed and an adjustment for minimum

[1] American Chemical Journal, *49*, 265, 1913.

[2] Physikalische Zeitschrift, *14*, 660, 1913.

deviation of one wave-length (*D*-line) held for all. The adjustment for minimum deviation was made in accord with Coblentz' description,[1] and a check on the adjustment was obtained by noting the position of the carbon dioxide band in the bunsen flame and the unchanged position of the selective reflection maximum of water at 3.20 μ during the observations.

Concerning the spectrometer, it may be mentioned, that the angle through which the prism table was rotated was measured with aid of telescope and scale, the tiny mirror being fastened to the top of the prism. The sensibility of the arrangement was such that 1 mm. on the scale corresponded to 1.5 minutes' rotation of the prism table. As one minute's rotation corresponds to about 0.12–0.15 μ in the investigated interval and the readings were made accurately to 0.1 mm., the accuracy in the wave-length determinations is about 0.01–0.02 μ.

The advantage of this way of determining the deviation over a direct reading on the spectrometer circle, lies in the possibility of the observer keeping as far away as possible from the heat-sensitive instrument during the observations. In the beginning and end of every observation series, the readings on the telescope scale were checked with the direct readings on the spectrometer circle. The spectrometer and the heat-measuring instrument, the radiometer, were both enclosed in a way that totally protected against air currents.

The Nichols' radiometer was surrounded by cotton and a blackened metal case, in the manner described by other observers. The mica vanes had a width of 0.80 mm., which corresponded to the same width of the spectrometer slit. The sensitiveness was such that a meter candle gave rise to a deflection of about 750 mm. The vacuum corresponded to maximum sensitiveness. The leak was so small that the sensitiveness remained practically the same during several days. When the writer returned after three months' absence, it was found that the sensitiveness of the radiometer had only diminished by 20 per cent. through increase of the pressure. Slight variations in the sensitiveness arose from temperature changes.

A 110-volt Nernst glower fed by the current from a 120-volt storage battery was used as source of radiation. The glower was well protected against air currents. The radiation was found to be constant within 1.5 per cent.

Method of Observing.

The following observation series were taken: (1) Reflection from a silvered plane mirror, whose reflecting power was assumed to be unity. (2) Reflection from the water surface. (3) Reflection from the solution.

[1] Coblentz, loc. cit., Part I.

In some cases a second determination of the energy distribution in the spectrum of the Nernst glower was made. This second determination gave, as a rule, results that agreed within 0–2 per cent. with the former determination.

The main purpose being to detect occurring shifts in the position of the reflection maximum, no attempt was made to measure the absolute value of the reflecting power.

RESULTS.

1. *Salts.*

Several solutions of different salts in water were investigated: NaCl, Na_2SO_4, KNO_3, $CuSO_4$, $SrCl_2$ and $CaCl_2$. Among these NaCl, Na_2SO_4, KNO_3 and $CuSO_4$ produced no shift in the position of the reflection maximum possible to detect. Fig. 1 shows the reflection curve of a

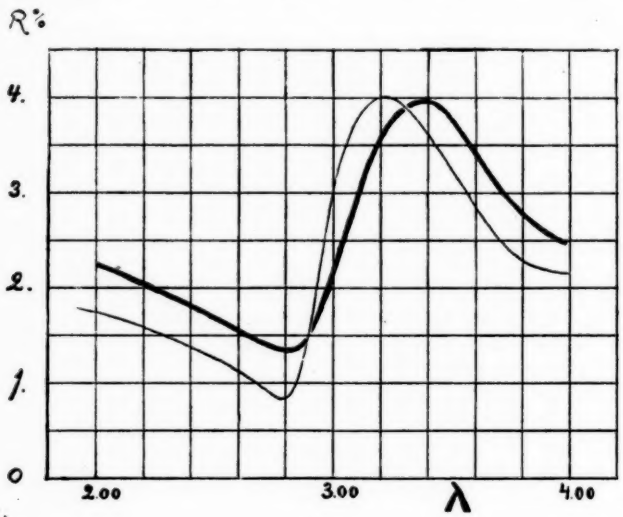

Fig. 1.

Light curve: Reflection from H_2O.
Heavy curve: Reflection from saturated solution of Na_2SO_4.

saturated solution of Glauber's salt as compared with the same curve for water. The selective characteristics are somewhat weakened but the position of the reflection maximum remains the same as for the pure solvent.

In the case of the strongly hydrated salts $SrCl_2$ and $CaCl_2$, the conditions are different. As the curves (Fig. 2) show, the selective properties have here been subjected to a considerable shift to the longer wavelengths. As both the maximum and the minimum are shifted by about

the same amount, the shift must be a consequence of a real change in the position of the absorption band.

Such a shift evidently corresponds to what is to be expected in the case

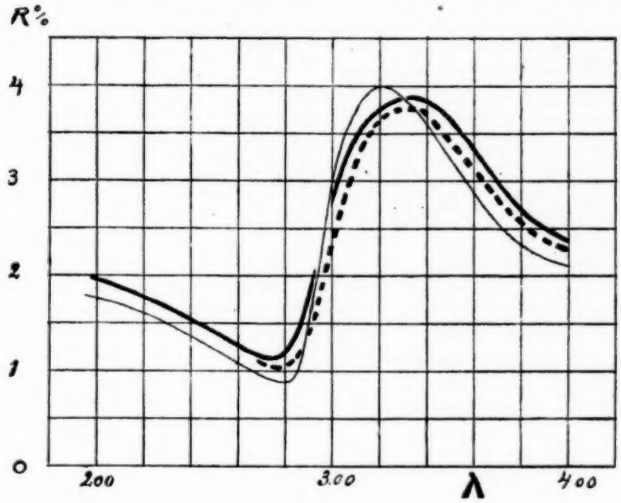

Fig. 2.

Light curve: Reflection from H_2O.
Heavy smooth curve: Reflection from saturated solution of $CaCl_2$.
Heavy dotted curve: Reflection from saturated solution of $SrCl_2$.

where a part of the water molecules combine with the dissolved substance to a dissolved hydrate. The hydroxyl-group is now combined with a positive radical of larger atomic weight than before, and analogous with the conditions of sulphates and carbonates, a shift to the longer wave-lengths is to be expected.

2. *Hydrates.*

After this result was obtained, it was found desirable to look for a similar shift in the cases where the dissolved substance is a real hydrate. For, when it has been shown that the same phenomenon occurs when known hydrates are dissolved in the water, the results obtained for the hydrated salts may be said to lead to a certain hypothesis. Consequently NaOH and KOH were investigated.

Figs. 3 and 4 give the results of an examination of concentrated solutions of sodium and potassium hydrate. The selective characteristics are evidently shifted to the longer wave-lengths by a considerable amount. For KOH the maximum occurs at 3.4 μ, for NaOH at 3.35 μ. For water the maximum and the minimum occur at 3.20 and 2.80 μ respectively.

3. $SO_2 \begin{matrix} —OH \\ —OH \end{matrix}$.

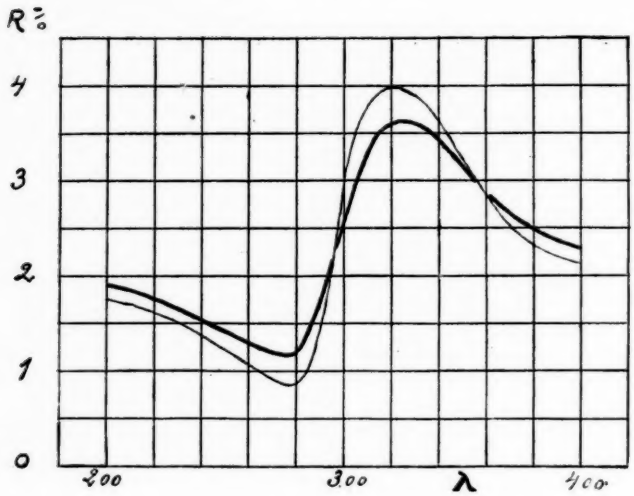

Fig. 3.

Light curve: Reflection from H_2O.
Heavy curve: Reflection from saturated solution of KOH.

Under certain conditions we may also regard sulphuric acid as a hydrate. As will be seen from Fig. 5 some interesting changes in the reflection properties occur when the acid is diluted.

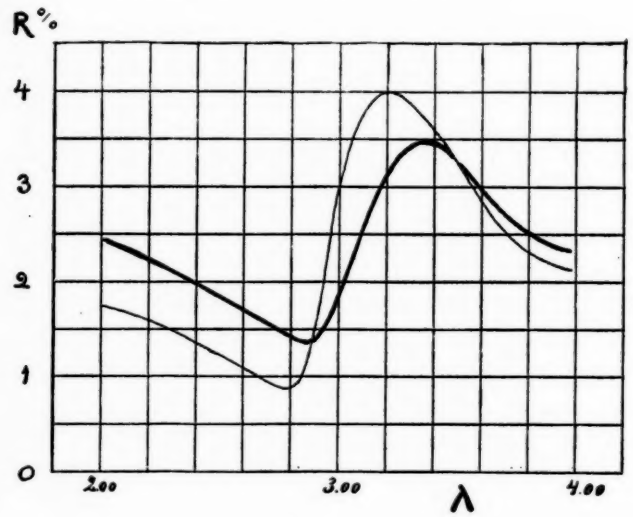

Fig. 4.

Light curve: Reflection from H_2O.
Heavy curve: Reflection from saturated solution of NaOH.

Fig. 5 shows the relation between reflected energy and deviation for various solutions of H_2SO_4 in water.[1] The reflection maximum decreases with an increase in the concentration. At the same time a considerable shift to the longer wave-length is noticed. When a concentration of about 75 per cent. is reached the reflection has a minimum. Between 75 per cent. and 100 per cent. the reflection maximum increases rapidly, showing that the concentrated acid has a marked reflection maximum at 3.55 μ corresponding to a strong absorption band at about 3.20 μ.

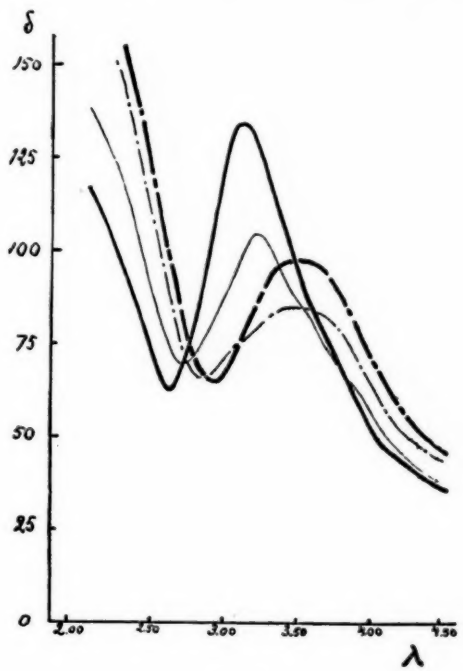

Fig. 5.

Heavy smooth curve: Energy reflected from H_2O.
Light smooth curve: Energy reflected from 32 per cent. $H_2SO_4 + H_2O$.
Light dotted curve: Energy reflected from 75 per cent. $H_2SO_4 + H_2O$.
Heavy dotted curve: Energy reflected from 98 per cent. H_2SO_4.

That sulphuric acid has a strong absorption band at about 3.20 μ, together with the fact that an absorption band at about 3.00 μ is characteristic of all compounds containing the hydroxide groups, seems to indicate that in the *undissociated sulphuric acid molecules* the hydrogen and oxygen are combined in such a way as to have the optical properties

[1] The form of the curve depends upon the energy distribution in the spectrum of the Nernst lamp.

of the hydroxide group. That the absorption band which in the case of water occurs at 3.0 μ is here somewhat shifted to the longer wave-lengths is only a natural consequence of the greater molecular weight of the acid.

The reflection curves show another interesting feature. It has been shown by Coblentz,[1] that the reflecting power of a compound in solution is practically proportional to the concentration, provided that no changes occur in the part of the molecule in which the mechanism giving rise to the reflection maximum is localized. If no such changes take place in the solution, the reflection power of the solution ought always to lie between the reflecting power of the constituents. From the data obtained from various solutions of sulphuric acid, it is obvious that the reflecting power of a 75 per cent. solution between the wave-lengths 3.2–3.6 μ is considerably less than the reflecting power of the constituents. At 3.28 μ, for instance, the reflecting power is only 85 against 105 for the water and 97 for the concentrated sulphuric acid. This disappearing of the reflection band reminds one strongly of similar conditions found by Pfund[2] for the reflection maxima of sulphuric acid at wave-lengths between 8 and 11 μ.

In our present case, it is interesting to notice this disappearing of the reflection maximum at 3.2 μ in connection with the generally accepted hypothesis that this band is due to the presence of the hydroxide group. In the undissociated H_2SO_4 molecules, the hydrogen and the oxygen are combined in such a way that it seems natural that they should show the optical properties of the hydroxide group. When the acid is dissolved in a dissociating solvent, the molecules are first broken down into H $H{\cdot}SO_4$ ions and finally into $H_2{\cdot}SO_4$ ions—complete change to the latter taking place at infinite dilution. The connection between the hydrogen and the oxygen forming the hydroxide group is consequently broken through the dissociation of the molecule. The concentration of the OH group—we consider the part furnished by the acid—is not proportional to the concentration of the acid, but decreases more rapidly with increased dilution. Such a dissociation process will evidently account for the observed weakening in the reflection maximum. We must, however, here take into consideration that the conditions probably are complicated through the formation of complexes, the acid molecules combining with the water molecules to dissolve hydrates. In such a process, similar to what we may suspect in the case of $SrCl_2$ and $CaCl_2$, a part of the water used as solvent is probably not present in the solution as water, but enters

[1] Coblentz, loc. cit., Part IV., p. 106.

[2] Loc. cit.

as a constituting part in a new compound that does not necessarily have the properties of its constituents.

Summary.

It has been shown in this paper:

1. That the selective reflection maximum of water at 3.20 μ is shifted to the longer wave-lengths when the strongly hydrated salts $CaCl_2$ and $SrCl_2$ are dissolved in the water.

2. That no appreciable shift occurs when NaCl, Na_2SO_4, KNO_3 and $CuSO_4$ are dissolved in the water.

3. That the reflection maximum is shifted by a considerable amount toward the longer waves when a real hydrate (NaOH, KOH) is in the solution.

4. That concentrated sulphuric acid shows the reflection maximum characteristic for the OH group.

5. That this maximum tends to vanish when the molecule is broken down through dissociation.

Cornell University,
November, 1913.

BENJAMIN OSGOOD PEIRCE

BENJAMIN OSGOOD PEIRCE, Hollis professor of mathematics and natural philosophy in Harvard University, Past-president of the American Physical Society and recent member of the editorial board of the PHYSICAL REVIEW, died at Cambridge, Massachusetts, on the fourteenth day of January, 1914, in his sixtieth year.

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

MINUTES OF THE SIXTY-NINTH MEETING.

THE regular Thanksgiving meeting of the Physical Society was held in Ryerson Physical Laboratory of the University of Chicago on Friday and Saturday, November 28 and 29, 1913.

The Friday afternoon session was in charge of a local committee consisting of R. A Millikan, A. A. Michelson and Henry Crew. The program consisted of the following symposium on the Quantum Theory:

The Quantum Theory and Radiation. C. E. MENDENHALL.

The Quantum Theory and Photoelectric Effect. R. A. MILLIKAN.

The Quantum Theory and Statistical Mechanics. MAX MASON.

The Quantum Theory and Atomic Structure. JACOB KUNZ.

The Quantum Theory and Specific Heats. A. C. LUNN.

The presentation of each topic was followed by a twenty-five-minute general discussion.

On Saturday there was both a forenoon and afternoon session and the following program of papers was presented. In the absence of president and vice-president, A. P. Carman was called to the chair and later R. A. Millikan.

The Relation between Photo-potentials and Frequency. W. H. KADESCH.

A Study of Contact P.D.'s between Metal Surfaces Prepared in Vacuo; the Effect of Ultra-violet Light upon these P.D.'s; and the Mutual Relation between Positive Potential and Contact P.D.'s. ALBERT E. HENNING.

Anomalous Temperature Effects upon Magnetized Steel. N. H. WILLIAMS.

Experimental Determination of the Earth's Rigidity. A. A. MICHELSON.

A New Maximum in the Wave Length Sensibility Curves of Selenium. F. C. BROWN and L. P. SIEG.

Evidence of a Diurnally Reversing Convectional Circulation of the Atmosphere Over the Upper Peninsula of Michigan. ERIC R. MILLER. (By title.)

Polarization of Long-wave Infra-red Radiation by Wire Gratings. A. D. COLE.

Glow Discharge in a Magnetic Field. R. F. EARHART.

A Polarization Spectrophotometer Using the Brace Prism. HARVEY B. LEMON.

Certain Experiments in Sound Diffraction. G. W. STEWART and HAROLD STILES.

Effect of Space Charge and Residual Gases on the Thermionic Current in High Vacuum. IRVING LANGMUIR.

Arrival Curves with Artificial Long Lines. CARL KINSLEY.

An Attempt at an Electromagnetic Emission Theory of Light. JACOB KUNZ.

Theory and Use of the Molecular Gauge. SAUL DUSHMAN.

A Modified Method of Measuring e/m and v for Cathode Rays. L. T. JONES.

An Experimental Determination of the Correction to the Law of Stokes for Falling Bodies, and of the Value of the Elementary Charge "e". JOHN Y. LEE.

On the Coefficient of Slip Between a Gas and a Liquid or Solid. R. A. MILLIKAN.

Note on the Electron Atmospheres (?). CARL R. ENGLAND.

Vapor Pressure of Molybdenum and Platinum. IRVING LANGMUIR.

Disappearance of Gas or Clean-up Effect in Vacuum Tubes. IRVING LANGMUIR.

A New Principle in the Application of Selenium to Photometry. F. C. BROWN and L. P. SIEG.

Determination of e/m from Measurements of Thermionic Currents. SAUL DUSHMAN.

Rate of Decay of Phosphorescence at Low Temperatures. E. H. KENNARD.

Determination of the Sun's Temperature. G. A. SHOOK. (By title.)

The Theory of Photoelectric and Photochemical Action. O. W. RICHARDSON. (By title.)

Photoelectric Potentials of Cathode Films. P. H. DIKE.

The Temperature Coefficient of Young's Modulus of an Iron Wire. H. L. DODGE.

The Temperature Distribution in an Incandescent Lamp Filament near a Cooling Junction. A. G. WORTHING.

Further Experiments on Magnetization by Angular Acceleration. S. J. BARNETT.

Production of Gases in Vacuum Tubes. G. WINCHESTER.

A Precision Relay. CARL KINSLEY.

A Thermopile of Bismuth Alloy. W. W. COBLENTZ.

ALFRED D. COLE,
Secretary.

A Thermopile of Bismuth Alloy.[1]

By W. W. Coblentz.

THE most recent investigation of Haken[2] and of Gelhoff and Neumeier[3] show that an alloy of Bi + 9 to 10 per cent. Sb gives a maximum E.M.F. which is of the order of 77 to 87 microvolts. The writer has found however that alloys containing more than 5 per cent. of antimony are too brittle for thermopiles. Moreover, different samples of this alloy supposed to contain the same amount of antimony did not give the same E.M.F., which varied from 61 to 85 microvolts. Apparently the physical structure has an influence upon the E.M.F. This alloy was therefore discarded, and pure bismuth was employed as in previous thermopiles. The best bismuth wire against silver gives an E.M.F. of 81 microvolts.

Tests showed that an alloy of bismuth containing 5 to 6 per cent. of tin gave a uniform (for different melts) value of 44 to 45 microvolts. A thermoelement consisting of the best bismuth and an alloy of Bi + 5 to 6 per cent. tin gives an E.M.F. of 125 to 127 microvolts per degree.

The bismuth (and in the near future, bismuth-tin alloy) may be obtained from Hartmann and Braun in fine pliable wire from 0.06 to .10 mm. diameter. This may be further reduced in size by cutting the wire in short lengths and pressing it flat between plates of glass. These flat pieces are then cut into narrow strips of the desired width.

The wire of bismuth-tin alloy is not yet on the market. It is made by spattering the molten metal, by allowing it to drop from a height upon a smooth perfectly clean glass plate.[4] Pfund[5] goes a step further, and by hurling the molten metal over a glass plate produces much longer filaments. The spattered material is quite pliable. The wide strips increase the emissivity, so that for the same resistance of the round as compared with the flat material, the best width to balance emissivity and conductivity must be found by experiment.

A thermopile was constructed as shown in Fig. 1. The receivers are of platinum 0.005 mm. in thickness and 1.8 by 3.0 mm. in area. The bismuth wire is 0.1 mm. diameter; the alloy was selected and estimated of a slightly greater area of cross-section. The thermopile is constructed by melting a globule of pure tin (0.05 mm. diameter) to the receiver by means of soldering solution. The receivers are then glued upon a piece of cardboard; properly spaced as shown in Fig. 1. The bismuth wire (joined to the silver wire by means of tin as described in previous publications) is joined to the tin on the receivers. The wires of bismuth-tin alloy are then placed on the receivers (see Fig. 1) and secured with Wood's alloy, care being taken that the fusible alloy does not affect the bismuth wire, thus producing a brittle juncture. The cardboard

[1] Abstract of a paper presented at the Chicago meeting of the Physical Society.

[2] Haken Vesh, Phys. Gesell., 12, p. 229, 1910.

[3] Gelhoff and Neumeier, Phys. Gesell., 15, p. 876, 1913.

[4] Coblentz, Bull. Bur. Standards, 7, p. 248, 1910.

[5] Pfund, Phys. Rev., 34, p. 228, 1912.

is then placed over the holder, the end-wires are attached to the binding posts by means of Wood's alloy and the card is removed by soaking in water. The front side of the receivers is painted with a mixture of lamp black and chemically precipitated platinum black, as previously described.[1]

The wires are joined in series-parallel thus reducing the resistance by one fourth from what would be obtained by joining all the elements in series. The silver or copper end-wire is used for three purposes: (1) to maintain a low resistance, (2) to maintain symmetry by having all the E.M.F. junctions close together, freely in contact with the air, (3) greater strength. The bismuth

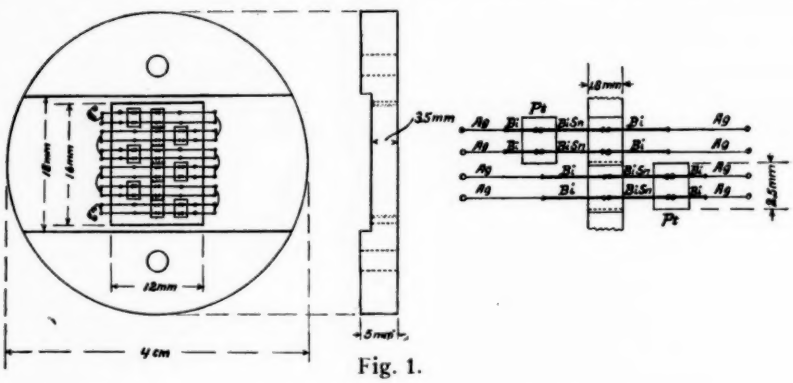

Fig. 1.

wire cannot be easily attached to binding posts, and although pliable it is not advisable to subject it to torsional strains. The additional length of wire (of negligible resistance) at the ends of the bismuth adds pliability which is needed in a commercial instrument, subjected to rough usage. No shellac is used except for covering the silver wire and for insulation at the overlapping edges of the central line of receivers. This produces a very quick acting instrument.

The radiation sensitivity of this thermopile was not quite as high as was hoped to attain. However, as a first attempt at this design, the knowledge gained indicates where improvements may be made. The resistance was 3.8 ohms. The thermal sensitivity was about 55 per cent. greater than the bismuth silver thermopile. The radiation sensitivity was 30 to 31 per cent. greater than the average sensitivity of a number of bismuth-silver thermopiles. For some researches it will therefore be of advantage to construct a thermopile of bismuth and of bismuth-tin alloy.

The efficiency of these thermopiles is such that one microwatt of radiant energy produces a rise in temperature of 15 to 16 $\times$ 10^{-5} degree in the receiver. The E.M.F. developed depends upon the number of junctions attached to the receiver and their manner of connection; whether all in series or in series-parallel as in this design. The voltage test was made with a Leeds and Northrup "type K" potentiometer, having a 100th shunt so that one division on the slide wire represents one microvolt, the standard lamp being at a distance of two meters. From this it may be seen that this type of thermopile may be

[1] Coblentz, Bull. Bur. Standards, 9, p. 7, 1912.

used in photometric and other investigations with rather insensitive auxiliary apparatus.

WASHINGTON, D. C., November 21, 1913.

AN ATTEMPT AT AN ELECTROMAGNETIC EMISSION THEORY OF LIGHT.[1]

BY JACOB KUNZ.

THE phenomena of light in discussion are explained by means of the following fundamental assumptions:

1. Light arises from oscillating electric charges. Each charge is connected with its own electromagnetic field, which has a material physical existence. These atomic fields carry mass, momentum and energy with them.
2. Maxwell's equations hold for these fields.
3. The velocity of light is always $-$ C.
4. Only relative motions can be defined and detected.

A MODIFIED METHOD OF MEASURING e/m AND v FOR CATHODE RAYS.[1]

BY L. T. JONES.

THE method used is the result of an attempt to eliminate as nearly as possible the errors that accompany the experimental determination of e/m by the usual method of electrostatic and magnetic deflections. The tube through which the rays are passed is made by drawing a scratch on a slip of iron and pressing it against the upper of the two electrostatic plates. The undeflected beam thus passes at grazing incidence to this plate. The upper electrostatic plate has a piece of soft iron, of the same dimensions as that on which the scratch is drawn, inlaid in it so that the cathode beam while passing through the tube is wholly surrounded by iron.

This method differs from those ordinarily employed in the position of the photographic plate. This is placed flat on the lower electrostatic plate. Sufficient potential is applied to deflect the beam downward to strike it. The electrostatic deflection is thus constant and may be determined accurately. With the distance between the electrostatic plates small in comparison with their linear dimensions the deflected beam may be made to fall wholly within a uniform electrostatic field.

The magnetic field is furnished by a solenoid with its axis perpendicular to the surfaces of the electrostatic plates. The solenoid encloses the whole apparatus and is of such length that the field is uniform and its strength may be calculated.

The cathode beam when deflected by the electrostatic field alone produces a straight line parallel to the undeflected beam. When the magnetic field is applied this line is displaced to the right or left according to the direction of the magnetic field and takes the form of the arc of a circle.

The measurements taken from the photographic plate are the horizontal distance of travel of the electron and its corresponding magnetic displacement.

[1] Abstract of a paper presented at the Chicago meeting of the Physical Society.

The greatest source of error is in the measurement of the magnetic deflection which enters, as usual, to the second power. The other factors, with the exception of the dielectric constant of the photographic plate, may be very accurately determined. The dielectric constant of the glass enters the equation in such a way that any error in its value affects only very slightly the resulting value of e/m.

LABORATORY OF PHYSICS,
UNIVERSITY OF ILLINOIS, November 14, 1913.

CERTAIN EXPERIMENTS IN SOUND DIFFRACTION.[1]

BY G. W. STEWART AND HAROLD STILES.

THE experiments undertaken resulted in interesting confirmations of sound theory. The four cases studied were the diffraction about a sphere whose circumference is equal to the wave-length, the alterations in the intensity passing through a narrow slit when the dimensions of the slit are changed, the intensities obtained by diffraction through circular openings of different sizes, and the variation of the intensity with the number of circular openings, the size of each being the same.

In the first experiment, the distortion of the intensity distribution about the sphere, due to the absorption brought about by resonance, was eliminated and the experimental results agreed with the theoretical predictions within the limit of experimental error.

In the last three experiments the changes in the openings modified the resonance of the tube which conducted the sound to the measuring instrument, and there was introduced an error which could not be eliminated with the apparatus used. In spite of this fact, it was found that the theory for the slit which shows that the total intensity is much more sensitive to changes in the length of the slit than in the width, was satisfactorily verified within a reasonable limit. The experiments with the circular openings also showed that the "conductivity" of the opening was approximately proportional to the area and that with equal circular openings used simultaneously the conductivity was proportional to the square of the number of openings. The range of the experiments should be extended.

EVIDENCE OF A DIURNALLY REVERSING CONVECTIONAL CIRCULATION OF THE ATMOSPHERE OVER THE UPPER PENINSULA OF MICHIGAN.[1]

BY ERIC R. MILLER.

CLIMATIC maps show the following abnormalities in the upper peninsula of Michigan and northeastern Wisconsin: Heavy rainfall in the interior and light on the coasts and great range of temperature in the interior, with late frosts in fall and early in spring.

An explanation of these abnormalities is found in the hypothesis of a convectional circulation of the atmosphere arising from the unequal heating and cooling of adjacent bodies of land and water. The rainfall is ascribed to the

[1] Abstract of a paper presented at the Chicago meeting of the Physical Society.

dynamic cooling of a column of air ascending over the land by day; the great range of temperature and extreme susceptibility to frost, to excessive radiation of heat from the ground through unusually clear sky produced by dynamic warming, and evaporation of cloud, in the column descending over the land by night.

The winds and weather of the upper Lake Region are usually under the control of passing cyclones but statistical analysis of wind-records affords a verification of the foregoing hypothesis by showing the existence of a diurnally reversing component of the wind.

Anomalous Temperature Effects upon Magnetized Steel.[1]

By N. H. Williams.

SMITH and Guild, in experimenting with short steel rods of high carbon content, found that, upon heating the specimens, the magnetism was reversed in the neighborhood of 200° C. Their explanation ascribed the reversal to the difference in action of the self-demagnetizing field of the magnet upon the iron and the carbide components of the steel.

The present paper deals with experiments which suggest an entirely different explanation.

It is found that the reversal is dependent upon the method of magnetizing the rod and that it can be prevented entirely by preventing an oscillatory discharge through the magnetizing coil.

The Positive Potential in the Photo-Electric Effect.[1]

By W. H. Kadesch.

TWO main sources of error have been especially troublesome in work on the positive potential. These are due, first, to the relatively short range of frequencies to which the easily manageable metals are sensitive, and secondly, to the effect of ageing of surfaces, and of photo-electric fatigue. The use of the strongly electropositive metals as electrodes in this research made it possible, not only to illuminate with light of greater wave-length than has hitherto been used but also to expose a new surface with the greatest readiness whenever desired.

Cylindrical electrodes of sodium and potassium were fixed to the rim of a wheel which could be rotated by means of an electro-magnet, the shaft of the wheel carrying a soft iron armature. In the plane of the wheel, and at opposite ends of a diameter, were placed a Faraday cylinder, and an auger-like knife operated by means of a second electro-magnet. To make an observation the electrode was turned first toward the knife, by means of which a slice of any desired thickness was taken off, then toward the Faraday cylinder, in position to receive the illumination. The source light was a spark about 2 mm. in length between iron terminals. The analyzing device was a quartz spectrometer.

[1] Abstract of a paper presented at the Chicago meeting of the Physical Society.

The Faraday cylinder was joined to one pair of quadrants of an electrometer, while the electrode was given any desired potential by means of potentiometer scheme. The positive potential corresponding to any wave-length was determined, either by giving the electrode a potential just sufficient to prevent the escape of electrons, or by varying the potential applied and then plotting curves with this, and the corresponding photo-electric current, as cöordinates. In the former method fresh surfaces were frequently cut, especially when the balancing potential was approached. In the latter, for each potential applied the current given by surfaces of different age was determined, a fresh one being cut for each exposure. The current for zero age was then found by extrapolation. This precaution was found to be unnecessary, however, since the slope of the age-current curves fell to zero at the balancing potential.

The range of wave-lengths employed was that from 2155 to 3970 A.U. Longer waves could not be used, with the quartz arrangement, because of the small dispersion. The positive potential was found to vary directly as the frequency of the light. This relation is expressed by the equation,

$$V = kn - V_0.$$

The value of k found for sodium was 3.87, that for potassium 3.83. The true value is somewhat higher, every source of error tending to reduce the value given by experiment.

THE THEORY OF PHOTO-ELECTRIC AND PHOTO-CHEMICAL ACTION.[1]

BY O. W. RICHARDSON.

IN this paper it is shown that the following equations are valid for all substances at all temperatures:

$$\int_{\nu_0}^{\infty} \frac{F(\nu\nu_0)h\nu^3}{e^{\frac{h\nu}{RT}}-1}\left\{\varphi(\nu) - \frac{h\nu e^{\frac{h\nu}{RT}}}{e^{\frac{h\nu}{RT}}-1} - RT^2\frac{\partial \log F(\nu\nu_0)}{\partial T}\right\}d\nu = 0, \qquad (10)$$

$$\int_{\nu_0}^{\infty} \frac{F(\nu\nu_0)h\nu^3 d\nu}{e^{\frac{h\nu}{RT}}-1} = A_1 T^{\frac{1}{2}} e^{\int^T \frac{\omega}{RT^2}dT} = \Phi(T)e^{-\frac{h\nu_0}{RT}}, \qquad (16)$$

$$\int_{\nu_0}^{\infty} \frac{h\nu^3}{e^{\frac{h\nu}{RT}}-1}\left\{\frac{F(\nu\nu_0)}{RT}\left(\frac{\partial\omega}{\partial\nu_0}\right)_T + \frac{\partial F(\nu\nu_0)}{\partial\nu_0}\right\}d\nu = 0, \qquad (17)$$

$$\int_{\nu_0}^{\infty} \frac{\nu^3 T_\nu F(\nu\nu_0)}{e^{\frac{h\nu}{RT}}-1}h d\nu = 2RT\Phi(T)e^{-\frac{h\nu_0}{RT}}, \qquad (27)$$

where the notation is the same as in Phil. Mag., Vol. 24, p. 570 (1912), except that T is written for temperature instead of θ, $F(\nu\nu_0)$ is written for $\epsilon F(\nu)$, $\varphi(\nu)$ is the energy abstracted from the radiation by an atom which is liberated under the excitation of radiation of frequency ν and $\Phi(T)$ may be regarded as defined by the right-hand one of the two equations (16). ν_0 is the value of ν at which $F(\nu\nu_0)$ becomes zero.

[1] Abstract of a paper presented at the Chicago meeting of the Physical Society, November 29, 1913.

It is also shown that the following values of the functions involved are consistent with all of the equations (10), (16), (17) and (27), viz.:

$$\left.\begin{aligned} \varphi(\nu) &= h\nu, \text{ universally,} \\ F(\nu\nu_0) &= \frac{A_1 h}{R^2}\left(1 - e^{-\frac{h\nu}{RT}}\right)\frac{\nu - \nu_0}{\nu^3}, \quad \nu_0 < \nu < \infty, \\ T_\nu &= h(\nu - \nu_0), \\ h\nu_0 &= \omega - \tfrac{3}{2}RT, \\ \Phi(T) &= A_1 T^2. \end{aligned}\right\} \quad (43)$$

PALMER PHYSICAL LABORATORY, PRINCETON, N. J.

DETERMINATION OF e/m FROM MEASUREMENTS OF THERMIONIC CURRENTS.[1]

BY SAUL DUSHMAN.

IN a paper on "The Effect of Space Charge and Residual Gases on the Thermionic Current in High Vacuum,"[2] Dr. I. Langmuir has developed the following formula for the thermionic current from a heated filament to a coaxial cylindrical anode.

$$i = \frac{2\sqrt{2}}{9}\sqrt{\frac{e}{m}}\frac{V^{\frac{3}{2}}}{r} = \frac{k \cdot V^{\frac{3}{2}}}{r}. \quad (1)$$

The formula has been tested experimentally by measuring the thermionic currents from a heated tungsten filament 10 mils diameter to a molybdenum anode, 7.62 cm. long and 2.54 cm. diameter. All end corrections were avoided by making use of two auxiliary anodes over the ends of the filaments, on the guard-ring principle.

The glass tube containing these electrodes was thoroughly exhausted by means of a molecular pump, the tube being heated to 360° C. and liquid air interposed between it and the pump. The anodes were freed from gases by bombardment with electrons of high velocity. This was secured by applying a very high potential of four or five thousand volts to the heated filament (cathode) and molybdenum cylinders (anode).

After the electrodes had been treated in this manner it was found that the space charge formula given above held very accurately over the range of voltages tested: 35 to 130. In each case the filament was heated to a temperature so high that in accordance with the Richardson equation very much higher currents could be obtained (provided a sufficiently high voltage was used).

Substituting for e/m in the above equation, the most probable value, 1.76×10^7, the constant k becomes 14.6×10^{-3}, where i is expressed in milliamperes per cm. length, V in volts, and r in cms. The values of i actually obtained for different values of V agreed with those calculated by means of this value for k, to within one per cent. These results were obtained under conditions in which

[1] Abstract of a paper presented at the Chicago meeting of the Physical Society, November 29, 1913.

[2] PHYS. REV., December, 1913.

no attempt was made to secure a high degree of accuracy. It would therefore seem as if the above method ought to prove highly applicable for the determination of e/m with an accuracy perhaps greater than that obtainable by any other method.

THEORY AND USE OF THE MOLECULAR GAGE.[1]

BY SAUL DUSHMAN.

FURTHER details are given regarding the construction of the vacuum gage previously described by Dr. I. Langmuir.[2] The theory of the instrument is developed for both the case of low pressures and that of higher pressures. At low pressures where the mean free path is larger than the distance between the mica disc and rotating aluminum plate, the theory shows that the angle of torque of the mica disc is proportional to the rate of rotation of the aluminum plate and to the function $p\sqrt{M/RT}$, where p is the pressure, M the molecular weight of the gas, R the gas constant and T the absolute temperature.

The method of calibration and correction factors to be introduced are discussed in detail.

The instrument has been used to measure the vapor tension of mercury at room temperature, and that of ice at $-78°$, and results obtained in agreement with those previously obtained by other investigators.

The pressures obtainable with a Gaede molecular pump were also measured by means of this instrument. A liquid air trap was inserted between gage and pump and the regular ground joint connection was used.

The speed of the pump was maintained at 8,100 r.p.m. With a pressure of 10^{-2} mm. on the rough side, the best vacuum obtainable without using liquid air or heating the gage was 0.15 micron. But by heating the gage to 300° C. for one hour and putting a liquid air flask over the trap, it was found possible to obtain a vacuum which was certainly lower than 0.005 micron (the gage was not sensitive to any smaller pressure). Under these conditions it was possible to increase the pressure on the rough side to 0.1 mm., without increasing the pressure on the high vacuum side, and on increasing the rough side pressure to 19 mm., the pressure in pump had increased to only 0.3 micron, giving a value of 57,000 for the ratio of pressures.

THE TEMPERATURE DISTRIBUTION IN AN INCANDESCENT LAMP FILAMENT NEAR A COOLING JUNCTION.[1]

BY A. G. WORTHING.

THE differential equation representing the distribution of temperature in a uniform cylindrical filament heated by a steady electric current, on the assumption of a constant current density, is

[1] Abstract of a paper presented at the Chicago meeting of the Physical Society, November 29, 1913.

[2] PHYS. REV., April, 1913.

$$\frac{\partial^2 T}{\partial l^2}+\frac{\partial^2 T}{\partial r^2}+\frac{1}{r}\frac{\partial T}{\partial r}+\frac{1}{k}\frac{\partial k}{\partial T}\left[\left(\frac{\partial T}{\partial l}\right)^2+\left(\frac{\partial T}{\partial r}\right)^2\right]+\frac{i^2\rho}{k}=0,$$

where T represents temperature; l, distance parallel to the filament axis; r, radial distance; i. current density; ρ, resistivity, and k, thermal conductivity.

The assumption of a new scale of temperature, so chosen that the corresponding value for thermal conductivity is constant for all temperatures, enables one to rewrite the differential equation as

$$\frac{\partial^2 T'}{\partial l^2}+\frac{\partial^2 T'}{\partial r^2}+\frac{1}{r}\frac{\partial T'}{\partial r}+\frac{i^2\rho'}{k'}=0,$$

where T', ρ' and k' in the new system correspond to T, ρ and k in the original equation.

The above equation has been applied to a tungsten filament 0.25 mm. in diameter heated by a 6.4 amp. current to about 2440° K. (Kelvin) using the temperature scale of Mendenhall and Forsythe. In this instance the term $i^2\rho/k'$ has been found approximately proportional to T', that is,

$$\frac{i^2\rho'}{k'}=a^2T'.$$

The differential equation thus conditioned becomes linear and a particular solution may readily be found. The further working out of the problem consists in building up a series from such terms in such a fashion that the experimental and theoretical boundary conditions are satisfied.

The following table indicates some of the more interesting results:

Temperature Distribution near a Cooling Junction, in a 0.25 mm. Tungsten Filament Heated by a 6.4 Amp. Current.

Distance from the Cooling Junction in cm.	Surface Temperature in °K.	Angle at the Surface between Temperature Gradient and Filament Axis in Degrees.	Axial Component of the Temperature Gradient in Degrees per cm.	Temperature Difference between Axis and Surface in °C.
0.2	1764	0.18	2250	0.04
.7	2323	4.6	420	0.21
.2	2421	31	70	0.27
.7	2437	76	11.4	0.27
∞	2440	90	0.0	0.28

In any single filament the temperature variation from the axial temperature, across any right section, varies quite closely with the square of the radial distance. In different sized filaments of the same material operated under the same conditions at the same maximum temperature, the temperature differences between the axes and the surfaces in the neighborhood of that maximum temperature vary quite closely as the radii.

[1] Abstract of a paper presented at the Chicago meeting of the Physical Society.

PHYSICAL LABORATORY,
NATIONAL LAMP WORKS OF GENERAL ELECTRIC CO.,
NELA PARK, CLEVELAND, O.

THE ILLUMINATION-CURRENT RELATIONSHIP IN POTASSIUM PHOTO-ELECTRIC CELLS.[1]

BY HERBERT E. IVES.

IT has been commonly believed that the photo-electric current is directly proportional to the intensity of illumination. The relationship has been experimentally studied by Elster and Geitel, Lenard, Griffith and Richtmyer. Lenard concluded the relationship to be linear, although his results plot as a shallow curve, convex toward the illumination axis. Griffith found the curve to increase more rapidly than the illumination. Elster and Geitel and Richtmyer found the linear relation. On the assumption of this linear relation the photo-electric cell has been suggested as a physical photometer.

The problem of the present investigation was to develop absorbing screens to use with alkali metal cells, probably rubidium or cæsium, to reduce the wave-length sensibility to that of the normal eye.

After carefully determining the conditions under which the quadrant electrometer could be used to measure current, a number of potassium cells were constructed and studied. It was found that no two showed the same illumination-current relationship. When plotted, the results showed all varieties of curves, from convex to the illumination axis to concave. Further work with special cells showed this relationship to be a function of voltage, electrode distance and gas pressure.

The wave-length sensibility curves were different for the various cells, probably due to varying relative strength of the normal and selective effects.

It is concluded that the photo-electric cell, at least as at present made, is only applicable to photometry if accurately calibrated for every illumination intensity used. The application of absorbing screens to produce a visual luminosity curve sensibility is not feasible.

[1] Abstract of a paper presented at the Atlanta meeting of the American Physical Society, December 30, 1913.